A Review of Recent Experiments and Calculations Relevant to the Kinetics of the HF Laser[a)]

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A review of rate coefficients relevant to HF laser kinetics modeling is presented. The literature has been surveyed from the last published review in 1983 to the present. Updated HF Einstein emission coefficients are tabulated. Rate coefficients are categorized according to their role in the HF laser model: HF generation, reactive quenching, self-relaxation, $V-V$ energy transfer, vibrational relaxation by atoms and molecules, F_2 dissociation, and F atom recombination. In addition, a review of recent experiments and theoretical calculations relevant to the role of rotational nonequilibrium in HF lasers is presented. A list of recommended temperature dependent expressions for critical reaction rate coefficients is given. © *2001 American Institute of Physics.*

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1. Introduction

1.1. Motivation

The baseline High Energy Laser technology for the Space Based Laser program's Integrated Flight Experiment is the 2.7 μm fundamental HF laser. Since its invention in the mid-1960s, the HF laser system has been extensively studied and developed to the point where weapons-class devices are now being built. In fact, most of the research in the recent past has focused on large-scale laser technology demonstrations. Despite the enormous effort expended to accomplish this, a complete understanding of all facets of HF laser performance is still evolving and is not complete. For example, research continues into the role of reagent mixing and heat transfer between the fluids and the construction material of the device. Combustor instabilities and other complex, transient, fluid dynamical features also impede our understanding of the laser's performance.

The only way to achieve insight into the details of the HF laser is to employ computational fluid dynamical (CFD) codes which can integrate the complex fluid properties with the myriad chemical reactions that occur in the laser cavity. Unfortunately (although perhaps not surprisingly considering the complexity of the problem), CFD codes have had limited success at accurately modeling real HF laser systems. As a result, both the laser performance data and the reaction rate constants used to baseline the models have come under increased scrutiny in recent years. This scrutiny has uncovered serious questions about the kinetics package that have yet to be answered conclusively. These questions include the importance of rotational nonequilibrium, the magnitude of various quenching processes, the role of three body and heterogeneous fluorine atom recombination, and other fundamental properties such as Einstein coefficients.

1.2. Scope

In general, experimental and theoretical efforts in the past 1–2 decades to elucidate the detailed state-to-state processes have been neglected in order to pursue large-scale device engineering and testing. For example, there have been no significant changes to the kinetics package since 1982,[1–4] no new significant advances in HF laser diagnostics for at least 10 years, and no significantly new nozzle designs until very recently.[5]

For the reasons described above, designers of large-scale HF lasers rely on CFD codes to predict performance, interpret experimental results, and optimized starting conditions for their systems. However, a CFD code is only as good at predicting and modeling experimental results as the ensemble of temperature dependent rate constants it uses allows it to be. A high fidelity three-dimensional (3D) CFD code with a poor kinetic package is no more useful for design calculations than a 1D code that uses the premixed limit.

Unfortunately, it is often the case that CFD codes predictions do not agree with the experimental results. For example, the observed lasing spectrum or measured powers for multiple lines may differ significantly from the CFD code prediction. When this occurs, it has been common practice in the HF laser community to adjust the kinetics package to achieve agreement with the observation even if this results in rate constant values that are inconsistent with independently measured values.[6] It is our belief that the use of HF laser CFD codes to discern or evaluate fundamental reaction kinetics and dynamics by fitting laser data is an unreliable practice for many reasons. First, the measured power of a HF laser depends not only on the fundamental reaction kinetics, but also the unique 3D mixing processes, the 3D temperature gradients, and the 3D optical resonator. In some cases, the laser device never reaches thermal equilibrium, and the temperature at any given point in the reactor is time dependent. The reliability and utility of such data for establishing fundamental kinetic parameters is at the very least, questionable. Furthermore, 1D and 2D CFD codes, which by definition approximate 3D processes, are not proper tools for determining state-to-state rate constants that are independent of the dimensionality of the system. In fact, because HF laser performance is dominated by mixing it is does not seem possible to draw accurate, unambiguous conclusions about the merits of a kinetics package or individual rate constants from parameterized CFD studies of laser performance data when the CFD codes use approximate methods to model the mixing.

Because of the enormous inherent complexity of the HF laser system (which would require explicit calculations for nine or more vibrational levels with up to 30 rotational levels each) a complete state-to-state HF laser chemistry package is essentially impossible to achieve. Any reasonable HF kinetics package must include at least a few simplifications and/or assumptions, the importance of which (by definition) cannot be determined. In most cases, the CFD codes do not attempt to account for each and every rovibrational state independently and the rotational distribution is assumed to be Boltzmann or quasi Boltzmann. Furthermore, even if it were possible to perform a state-to-state calculation in a reasonable amount of computational time, the requisite state-to-state rate constants are not known and some kind of approximation must be made for the majority of relevant processes. In some cases it is impossible to assess the accuracy of the estimates. For example, the approximation that assumes rotational equilibrium of each vibrational manifold is often adopted to reduce the number of species that must be tracked, even though it is impossible to establish *quantitatively* how much error or uncertainty this introduces. In light of these inherent limitations, HF CFD codes should not be expected to reproduce experimental results with the kind of fidelity that is normally associated with kinetically simpler systems such as the chemical oxygen iodine laser.

The best course of action, in our opinion, is to use the best ensemble of independently measured rate constants with the best mixing and optical resonator models available to make *relative* performance predictions. Hence, the main focus of this paper is to review recent relevant experiments and theoretical calculations with the ultimate goal of establishing

the most rigorously correct and physically sound kinetics package possible.

With these issues in mind, the main topics of this paper (in order of their presentation) are Einstein coefficients and relevant kinetic measurements. It is not within the scope of this document to discuss fluid dynamics issues, such as recently developed 3D CFD codes or new algorithms to model mixing or optical resonators.

2. Experiments and Calculations Relevant to HF Laser Modeling

2.1. Einstein Coefficients

Two of the most important fundamental properties of a laser are the stimulated emission cross section and the small signal gain which are related by Eq. (1):

$$g = \sigma_{\text{stim}}(\nu)\left[N_u - \frac{g_u}{g_l}N_l\right], \tag{1}$$

where N_u, N_l, g_u, and g_l are the number densities and degeneracies for the upper and lower states, respectively, and $\sigma_{\text{stim}}(\nu)$ is the stimulated emission cross section. The stimulated emission cross section is a function of the Einstein emission coefficient $A_{nm}(\text{s}^{-1})$, transition frequency $\nu(\text{Hz})$, and the spectroscopic line shape $f(\nu)(\text{Hz}^{-1})$:

$$\sigma_{\text{stim}}(\nu) = \frac{c^2 A_{\text{nm}}}{8\pi\nu^2} * f(\nu). \tag{2}$$

The Einstein emission coefficient is tied directly to the quantum mechanical probability for a spontaneous transition from an upper n to a lower state m by

$$A_{nm} = \frac{64\pi^4\nu^3}{3h}\left(\frac{S_J}{g_u}\right)|R_{nm}|^2, \tag{3}$$

where $S_J = J_l + 1$ for an R branch or J_l for a P branch line, $g_u = 2J_u + 1$, and $|R_{nm}|^2$ is the square of the transition dipole matrix element:

$$|R_{nm}|^2 = \langle n|\mu|m\rangle^2 = \int \Psi_n^* \mu \Psi_m d\tau. \tag{4}$$

The Einstein coefficients used by most HF CFD codes are based on the values found in the *Handbook of Chemical Lasers*[7] (which are in turn, based on the empirical calculations of Herbelin and Emanuel),[8] and have not been updated in over 25 years. Table 1 gives a representative sample of the Handbook's HF vibration–rotational Einstein emission coefficients as well as the more recent (and preferred) results of Setser and co-workers,[9] see below. While the agreement is generally good for the first three vibrational levels, large differences are apparent as v and J increase.

It is possible to calculate Einstein coefficients from first principles with an accurate potential energy surface and a suitable dipole moment function. Until recently, *ab initio* potential functions have not been readily available. As a result, semiempirical Morse or RKR (Rydberg–Klein–Rees) potential functions have been traditionally used. For low to

TABLE 1. HF$(v,J)P$ branch Einstein A coefficients (s^{-1})

v_{lower}	J_{lower}	Handbook of Chemical Lasers[a]	Arunan, Setser, and Ogilvie[b]
0	1	193.16	199.28
	3	120.18	123.93
	6	113.15	116.75
	9	111.22	115.02
	12	108.66	112.82
	15	104.60	109.24
	18	98.96	104.13
	21	91.94	97.60
1	1	329.55	342.84
	3	205.78	213.70
	6	194.52	201.73
	9	191.72	198.86
	12	187.56	194.93
	15	180.61	188.37
	18	170.73	179.01
	21	158.30	167.10
2	1	414.99	435.24
	3	260.27	272.09
	6	247.24	257.58
	9	244.45	254.25
	12	239.55	249.20
	15	230.71	240.50
	18	217.84	227.98
	21	201.45	212.01
3	1	455.20	482.57
	3	287.07	302.76
	6	274.37	287.70
	9	272.32	284.59
	12	267.37	279.14
	15	257.53	269.23
	18	242.76	254.75
	21	223.71	236.20
4	1	456.19	493.15
	3	289.72	310.80
	6	279.03	296.82
	9	278.27	294.56
	12	273.84	289.40
	15	263.76	279.23
	18	248.07	263.95
	21	227.54	244.17
5	1	424.47	475.83
	3	272.06	301.59
	6	264.62	289.98
	9	265.52	289.20
	12	262.02	285.10
	15	252.34	275.63
	18	236.59	260.71
	21	215.69	240.99
6	1	367.41	439.78
	3	238.41	280.67
	6	234.96	272.27
	9	237.63	273.57
	12	235.35	271.37
	15	226.58	263.68
	18	211.57	250.38
	21	191.32	232.05
7	1	293.41	395.24
	3	193.70	254.25
	6	194.38	249.52
	9	198.74	253.53
	12	197.80	254.23
	15	190.36	249.58
	18	176.78	239.27
	21	158.13	223.67

[a]See Ref. 7.
[b]See Ref. 9

moderate v levels ($v < 10$), the RKR and Morse potentials give comparable results. The RKR function more correctly reproduces the dissociation behavior and it is especially useful for this molecule. In general, however, the dipole moment function $\mu(R)$ has greater influence on the matrix elements R_{nm} than does the form of the potential. In most cases, a truncated Taylor series expansion about the internuclear separation gives satisfactory results for the dipole moment function

$$\mu(R) = \sum_i M_i (R - R_e)^i, \qquad (5)$$

where M_i are determined by experimental measurements of the intensity of overtone transitions.[10] Because the data are limited, it is generally necessary to extrapolate $\mu(R)$ for R values that are not observed experimentally. Typically, semi-empirical techniques, such as the Padé expansion of Herbelin and Emanuel,[8] have been used to perform this extrapolation.

In 1991, Zemke[11] and co-workers published a potential surface based on the spectroscopically determined potential of Coxon and Hajigeorgiou,[12] adjusted to reproduce the proper long-range behavior by including both dispersion and exchange effects.[13] In the same publication, Zemke and co-workers provided an *ab initio* dipole moment function that spanned the same range of internuclear distances as the complete potential energy curve. The resulting Einstein coefficients should be the most reliable theoretical values. Shortly after the publication of Zemke's results, Setser and co-workers produced an extensive set of vibration–rotational Einstein A coefficients for HF/DF and HCl/DCl.[9] Their calculations used an RKR potential and the *ab initio* dipole moment function of Ogilvie.[14] Their results are in excellent agreement with Zemke, as shown in Table 2. For purposes of comparison, the Einstein coefficients calculated by Herbelin and Emanuel[8] and Sileo and Cool[10] are also shown in Table 2. In the latter case an RKR potential was used with their own experimentally determined dipole moment function, while the former used a Morse potential function and a Padé expansion fit to the data of Sileo and Cool. The agreement at low v levels is quite good for all methods, but begins to decay at higher vibrational quantum numbers.

Considering the importance of the Einstein A coefficients in calculating the stimulated emission cross section and the gain, the most accurate values available should be employed. Unfortunately, Zemke and co-workers calculations were only for a limited number of rotational quantum numbers. We recommend that the HF CFD codes be updated with the results of Arunan et al.[9]

2.2. HF Kinetics

Most modern day HF CFD codes have kinetics packages that are based on a 1976 Aerospace Corporation technical report by Cohen and Bott[1] This article and its 1977 supplement[2] contained a thorough review of contemporary literature results up to 1977 and recommendations for rate constants related to the HF laser. An update was published 5

TABLE 2. HF fundamental and overtone Einstein emission coefficients

Transition	Herbelin and Emanuel[a]	Sileo and Cool[b]	Arunan, Setser, and Ogilvie[c]	Zemke *et al.*[d]
		$\Delta v = -1$		
1–0	188.6	189	194.5	203.5
2–1	319.8	324	333.9	348.4
3–2	398.3	410	422.8	439.9
4–3	429.7	453	467.7	484.1
5–4	421.3	460	477.2	487.2
6–5	381.1	436	459.8	455.9
7–6	318.6	386	425.4	397.7
8–7	243.7	317	354.6	320.9
9–8	166.9	236	269.8	235.2
		$\Delta v = -2$		
2–0	23.4	23.6	23.5	24.7
3–1	67.9	66.2	65.9	70.7
4–2	130.5	124	123.5	134.2
5–3	207.0	193	191.2	212.3
6–4	291.9	271	262.3	301.9
7–5	378.3	354	328.0	399.9
8–6	457.8	443	429.1	501.3
9–7	520.9	536	531.9	599.8
		$\Delta v = -3$		
3–0	1.2	1.6	1.5	1.6
4–1	4.8	6.1	5.5	5.9
5–2	12.2	14.4	13.1	13.9
6–3	25.0	27.0	25.4	26.1
7–4	44.5	43.9	44.9	43.3
8–5	72.4	64.8	···	66.5
9–6	109.5	89.1	···	96.7

[a]See Ref. 8.
[b]See Ref. 10.
[c]See Ref. 9.
[d]See Ref. 11.

years later in 1982,[3] and a few relevant reactions were reviewed again in 1983 by Cohen and Westberg.[4] Beyond these reports, there have only been a handful of critical evaluations of kinetic data relevant to the HF laser. A 1982 review article by Leone summarizes hydrogen halide vibrational energy transfer and contains rate coefficients relevant to the HF laser system.[15] In 1983, George Hart of the Naval Research Laboratory reviewed the pulsed DF chemical laser codes and the corresponding kinetic database.[16] Although his report was specifically for DF, it contains a wide variety of relevant and helpful evaluations for the HF laser. Tables 3 and 4 summarize the 1977 and 1982 Cohen and Bott packages. For purposes of clarity, the very extensive HF laser reaction mechanism is organized into broad categories such as HF generation, reactive quenching, energy transfer, etc. The two kinetic packages shown are quite similar or identical in some respects, but differ significantly for a number of critical reactions. The following paragraphs summarize the current status of each category and evaluate the rate constants relative to the most recent experimental measurements and theoretical calculations.

2.2.1. HF Generation—H+F$_2$ and F+H$_2$

2.2.1.1. H+F$_2$

The generation of HF(v) in the HF laser can proceed via one of two reactions, H+F$_2$ or F+H$_2$, which have signifi-

TABLE 3. HF rate package comparison—rate constant expressions

Category	Reaction	Rate constant expression[a]	
		Cohen and Bott[2,b]	Cohen and Bott[3,c,d]
HF generation	$F+H_2(0)\rightarrow HF(1)+H$	$2.72\times10^{13}e^{-1.6/RT}$	$3.90\times10^{11}T^{0.5}e^{-0.61/RT}$
	$F+H_2(0)\rightarrow HF(2)+H$	$8.79\times10^{13}e^{-1.6/RT}$	$1.43\times10^{12}T^{0.5}e^{-0.61/RT}$
	$F+H_2(0)\rightarrow HF(3)+H$	$4.48\times10^{13}e^{-1.6/RT}$	$7.80\times10^{11}T^{0.5}e^{-0.61/RT}$
	$H+F_2\rightarrow HF(3)+F$	$9.60\times10^{12}e^{-2.4/RT}$	$2.1\times10^{8}T^{1.5}e^{-1.68/RT}$
	$H+F_2\rightarrow HF(4)+F$	$1.56\times10^{13}e^{-2.4/RT}$	$3.9\times10^{8}T^{1.5}e^{-1.68/RT}$
	$H+F_2\rightarrow HF(5)+F$	$4.20\times10^{13}e^{-2.4/RT}$	$6.9\times10^{8}T^{1.5}e^{-1.68/RT}$
	$H+F_2\rightarrow HF(6)+F$	$5.28\times10^{13}e^{-2.4/RT}$	$9.9\times10^{8}T^{1.5}e^{-1.68/RT}$
	$H+F_2\rightarrow HF(7)+F$	0	$4.5\times10^{8}T^{1.5}e^{-1.68/RT}$
	$H+F_2\rightarrow HF(8)+F$	0	$3.6\times10^{8}T^{1.5}e^{-1.68/RT}$
Reactive quenching	$H+HF(3)\rightarrow H_2(0)+F$	$1.62\times10^{13}T^{-0.01}e^{-0.835/RT}$	$1.8\times10^{13}T^{0.179}e^{-0.760/RT}$
	$H+HF(4)\rightarrow H_2(0)+F$	$8.50\times10^{11}e^{-0.46/RT}$	$3.0\times10^{13}e^{-0.5/RT}$
	$H+HF(5)\rightarrow H_2(0)+F$	$3.96\times10^{12}e^{-0.51/RT}$	$3.0\times10^{13}e^{-0.5/RT}$
	$H+HF(6)\rightarrow H_2(0)+F$	$4.18\times10^{12}e^{-0.58/RT}$	$3.0\times10^{13}e^{-0.5/RT}$
	$H+HF(4)\rightarrow H_2(1)+F$	$8.50\times10^{11}e^{-0.46/RT}$	$3.0\times10^{13}e^{-0.5/RT}$
	$H+HF(5)\rightarrow H_2(1)+F$	$7.04\times10^{12}e^{-0.51/RT}$	$6.0\times10^{13}e^{-0.5/RT}$
	$H+HF(6)\rightarrow H_2(1)+F$	$4.18\times10^{12}e^{-0.58/RT}$	$3.0\times10^{13}e^{-0.5/RT}$
	$H+HF(6)\rightarrow H_2(2)+F$	$1.06\times10^{13}e^{-0.58/RT}$	$9.0\times10^{13}e^{-0.5/RT}$
Self-relaxation of HF (quenching by ground state HF)	$HF(1)+HF\rightarrow HF(0)+HF$	k_0	$k_0=(3.5\times10^4T^{2.26}+2.95\times10^{14}T^{-1})$
	$HF(2)+HF\rightarrow HF(1)+HF$	$4\,k_0$	$6.06\,k_0$
	$HF(3)+HF\rightarrow HF(2)+HF$	$6\,k_0$	$17.4\,k_0$
	$HF(4)+HF\rightarrow HF(3)+HF$	$3\,k_0$	$36.8\,k_0$
	$HF(5)+HF\rightarrow HF(4)+HF$	$10\,k_0$	$65.7\,k_0$
	$HF(6)+HF\rightarrow HF(5)+HF$	$14\,k_0$	$105.5\,k_0$
	$HF(2)+HF\rightarrow HF(0)+HF$	$2\,k_0$	0
	$HF(3)+HF\rightarrow HF(1)+HF$	$1.5\,k_0$	0
	$HF(4)+HF\rightarrow HF(2)+HF$	$3\,k_0$	0
	$HF(5)+HF\rightarrow HF(3)+HF$	$5\,k_0$	0
	$HF(6)+HF\rightarrow HF(4)+HF$	$7\,k_0$	0
	$HF(3)+HF\rightarrow HF(0)+HF$	$1.5\,k_0$	0
	$HF(4)+HF\rightarrow HF(1)+HF$	$3\,k_0$	0
	$HF(5)+HF\rightarrow HF(2)+HF$	$5\,k_0$	0
	$HF(6)+HF\rightarrow HF(3)+HF$	$7\,k_0$	0
	$HF(7)+HF\rightarrow HF(4)+HF$	0	0
	$HF(4)+HF\rightarrow HF(0)+HF$	$3\,k_0$	0
	$HF(5)+HF\rightarrow HF(1)+HF$	$5\,k_0$	0
	$HF(6)+HF\rightarrow HF(2)+HF$	$7\,k_0$	0
	$HF(5)+HF\rightarrow HF(0)+HF$	$5\,k_0$	0
	$HF(6)+HF\rightarrow HF(1)+HF$	$7\,k_0$	0
	$HF(6)+HF\rightarrow HF(0)+HF$	$7\,k_0$	0
HF V–V energy transfer	$HF(1)+HF(1)\rightarrow HF(2)+HF(0)$	$3.6\times10^{15}T^{-1}$	$4.59\times10^{15}T^{-1}$
	$HF(2)+HF(2)\rightarrow HF(3)+HF(1)$	$1.5\times10^{15}T^{-1}$	$4.11\times10^{15}T^{-1}$
	$HF(3)+HF(3)\rightarrow HF(4)+HF(2)$	$1.0\times10^{15}T^{-1}$	$4.55\times10^{15}T^{-1}$
	$HF(4)+HF(4)\rightarrow HF(5)+HF(3)$	$7.5\times10^{14}T^{-1}$	$4.92\times10^{15}T^{-1}$
	$HF(5)+HF(5)\rightarrow HF(6)+HF(4)$	$6.0\times10^{14}T^{-1}$	$5.24\times10^{15}T^{-1}$
	$HF(6)+HF(6)\rightarrow HF(7)+HF(5)$	$5.0\times10^{14}T^{-1}$	$5.53\times10^{15}T^{-1}$
	$HF(1)+HF(2)\rightarrow HF(0)+HF(3)$	$1.8\times10^{15}T^{-1}$	$5.29\times10^{15}T^{-1}$
	$HF(1)+HF(3)\rightarrow HF(0)+HF(4)$	$1.2\times10^{15}T^{-1}$	$5.85\times10^{15}T^{-1}$
	$HF(1)+HF(4)\rightarrow HF(0)+HF(5)$	$9.0\times10^{14}T^{-1}$	$6.32\times10^{15}T^{-1}$
	$HF(1)+HF(5)\rightarrow HF(0)+HF(6)$	$7.2\times10^{14}T^{-1}$	$6.74\times10^{15}T^{-1}$
	$HF(1)+HF(6)\rightarrow HF(0)+HF(7)$	$6.0\times10^{14}T^{-1}$	$7.11\times10^{15}T^{-1}$
	$HF(2)+HF(3)\rightarrow HF(1)+HF(4)$	$1.0\times10^{15}T^{-1}$	$4.55\times10^{15}T^{-1}$
	$HF(2)+HF(4)\rightarrow HF(1)+HF(5)$	$7.5\times10^{14}T^{-1}$	$4.92\times10^{15}T^{-1}$
	$HF(2)+HF(5)\rightarrow HF(1)+HF(6)$	$6.0\times10^{14}T^{-1}$	$5.24\times10^{15}T^{-1}$
	$HF(2)+HF(6)\rightarrow HF(1)+HF(7)$	$5.0\times10^{14}T^{-1}$	$5.53\times10^{15}T^{-1}$
	$HF(3)+HF(4)\rightarrow HF(2)+HF(5)$	$7.5\times10^{14}T^{-1}$	$4.92\times10^{15}T^{-1}$
	$HF(3)+HF(5)\rightarrow HF(2)+HF(6)$	$6.0\times10^{14}T^{-1}$	$5.24\times10^{15}T^{-1}$
	$HF(3)+HF(6)\rightarrow HF(2)+HF(7)$	$5.0\times10^{14}T^{-1}$	$5.53\times10^{15}T^{-1}$
	$HF(4)+HF(5)\rightarrow HF(3)+HF(6)$	$6.0\times10^{14}T^{-1}$	$5.24\times10^{15}T^{-1}$
	$HF(4)+HF(6)\rightarrow HF(3)+HF(7)$	$5.0\times10^{14}T^{-1}$	$5.53\times10^{15}T^{-1}$
	$HF(5)+HF(6)\rightarrow HF(4)+HF(7)$	$5.0\times10^{14}T^{-1}$	$5.53\times10^{15}T^{-1}$

TABLE 3. HF rate package comparison—rate constant expressions—Continued

		Rate constant expression[a]	
Category	Reaction	Cohen and Bott[2,b]	Cohen and Bott[3,c,d]
	$HF(0)+H_2(1)\rightarrow HF(1)+H_2(0)$	8.0×10^{11}	$2.40\times10^{10}T^{0.5}e^{+0.407/RT}$
	$HF(1)+H_2(1)\rightarrow HF(2)+H_2(0)$	1.6×10^{12}	$3.06\times10^{10}T^{0.5}e^{+0.407/RT}$
	$HF(2)+H_2(1)\rightarrow HF(3)+H_2(0)$	2.4×10^{12}	$3.53\times10^{10}T^{0.5}e^{+0.407/RT}$
	$HF(3)+H_2(1)\rightarrow HF(4)+H_2(0)$	3.2×10^{12}	$3.90\times10^{10}T^{0.5}e^{+0.407/RT}$
	$HF(4)+H_2(1)\rightarrow HF(5)+H_2(0)$	4.0×10^{12}	$4.22\times10^{10}T^{0.5}e^{+0.407/RT}$
	$HF(5)+H_2(1)\rightarrow HF(6)+H_2(0)$	4.8×10^{12}	$4.49\times10^{10}T^{0.5}e^{+0.407/RT}$
	$HF(0)+H_2(2)\rightarrow HF(1)+H_2(1)$	8.0×10^{11}	0
	$HF(1)+H_2(2)\rightarrow HF(2)+H_2(1)$	1.6×10^{12}	0
	$HF(2)+H_2(2)\rightarrow HF(3)+H_2(1)$	2.4×10^{12}	0
Vibrational	$HF(3)+H_2(2)\rightarrow HF(4)+H_2(1)$	3.2×10^{12}	0
energy transfer	$HF(4)+H_2(2)\rightarrow HF(5)+H_2(1)$	4.0×10^{12}	0
from $H_2(1-3)$	$HF(5)+H_2(2)\rightarrow HF(6)+H_2(1)$	4.8×10^{12}	0
	$HF(0)+H_2(2)\rightarrow HF(2)+H_2(0)$	1.6×10^{12}	0
	$HF(1)+H_2(2)\rightarrow HF(3)+H_2(0)$	2.4×10^{12}	0
	$HF(2)+H_2(2)\rightarrow HF(4)+H_2(0)$	3.2×10^{12}	0
	$HF(3)+H_2(2)\rightarrow HF(5)+H_2(0)$	4.0×10^{12}	0
	$HF(4)+H_2(2)\rightarrow HF(6)+H_2(0)$	4.8×10^{12}	0
	$HF(0)+H_2(3)\rightarrow HF(3)+H_2(0)$	2.4×10^{12}	0
	$HF(1)+H_2(3)\rightarrow HF(4)+H_2(0)$	3.2×10^{12}	0
	$HF(2)+H_2(3)\rightarrow HF(5)+H_2(0)$	4.0×10^{12}	0
	$HF(3)+H_2(3)\rightarrow HF(6)+H_2(0)$	4.8×10^{12}	0
	$HF(1)+H_2\rightarrow HF(0)+H_2$	$6.0\times10^{7}T$	$k_0=(6.0\times10^{11}T^{-1}+1\times10^{4}T^{2.28})$
	$HF(2)+H_2\rightarrow HF(1)+H_2$	$1.2\times10^{8}T$	$6.5\,k_0$
Collisional	$HF(3)+H_2\rightarrow HF(2)+H_2$	$1.8\times10^{8}T$	$19.4\,k_0$
relaxation	$HF(4)+H_2\rightarrow HF(3)+H_2$	$2.4\times10^{8}T$	$42.2\,k_0$
of HF	$HF(5)+H_2\rightarrow HF(4)+H_2$	$3.0\times10^{8}T$	$77.1\,k_0$
by H_2	$HF(6)+H_2\rightarrow HF(5)+H_2$	$3.6\times10^{8}T$	$126.2\,k_0$
	$HF(7)+H_2\rightarrow HF(6)+H_2$	$4.2\times10^{8}T$	0
	$HF(1)+H\rightarrow HF(0)+H$	$1.5\times10^{12}e^{-0.7/RT}$	$4.0\times10^{11}e^{-0.7/RT}$
	$HF(2)+H\rightarrow HF(1)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(3)+H\rightarrow HF(2)+H$	$5.4\times10^{14}e^{-0.7/RT}$	$1.4\times10^{16}T^{-1}$
	$HF(4)+H\rightarrow HF(3)+H$	$5.4\times10^{14}e^{-0.7/RT}$	$2.0\times10^{16}T^{-1}$
	$HF(5)+H\rightarrow HF(4)+H$	$5.4\times10^{14}e^{-0.7/RT}$	$2.7\times10^{16}T^{-1}$
	$HF(6)+H\rightarrow HF(5)+H$	$5.4\times10^{14}e^{-0.7/RT}$	$3.5\times10^{16}T^{-1}$
	$HF(7)+H\rightarrow HF(6)+H$	0	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(2)+H\rightarrow HF(0)+H$	$2.7\times10^{12}e^{-0.7/RT,b}$	$7.0\times10^{11}e^{-0.7/RT,d}$
	$HF(3)+H\rightarrow HF(1)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(4)+H\rightarrow HF(2)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
Collisional	$HF(5)+H\rightarrow HF(3)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
relaxation	$HF(6)+H\rightarrow HF(4)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
of HF	$HF(7)+H\rightarrow HF(5)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
by H atoms	$HF(3)+H\rightarrow HF(0)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(4)+H\rightarrow HF(1)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(5)+H\rightarrow HF(2)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(6)+H\rightarrow HF(3)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(7)+H\rightarrow HF(4)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(4)+H\rightarrow HF(0)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(5)+H\rightarrow HF(1)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(6)+H\rightarrow HF(2)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(5)+H\rightarrow HF(0)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(6)+H\rightarrow HF(1)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$
	$HF(6)+H\rightarrow HF(0)+H$	$2.7\times10^{12}e^{-0.7/RT}$	$7.0\times10^{11}e^{-0.7/RT}$

TABLE 3. HF rate package comparison—rate constant expressions—Continued

Category	Reaction	Rate constant expression[a]	
		Cohen and Bott[2,b]	Cohen and Bott[3,c,d]
Collisional relaxation of HF by M	HF(1)+M→HF(0)+M	$7.70\times10^{-7}T^5$ [M=F$_2$, Ar]	$2.0\times10^{-5}T^{4.5}$ [M=F$_2$, Ar]
	HF(2)+M→HF(1)+M	$1.54\times10^{-6}T^5$ [M=F$_2$, Ar]	$1.3\times10^{-4}T^{4.5}$ [M=F$_2$, Ar]
	HF(3)+M→HF(2)+M	$2.31\times10^{-6}T^5$ [M=F$_2$, Ar]	$3.88\times10^{-4}T^{4.5}$ [M=F$_2$, Ar]
	HF(4)+M→HF(3)+M	$3.08\times10^{-6}T^5$ [M=F$_2$, Ar]	$8.44\times10^{-4}T^{4.5}$ [M=F$_2$, Ar]
	HF(5)+M→HF(4)+M	$3.85\times10^{-6}T^5$ [M=F$_2$, Ar]	$1.54\times10^{-3}T^{4.5}$ [M=F$_2$, Ar]
	HF(6)+M→HF(5)+M	$4.62\times10^{-6}T^5$ [M=F$_2$, Ar]	$2.52\times10^{-3}T^{4.5}$ [M=F$_2$, Ar]
	HF(7)+M→HF(6)+M	$5.39\times10^{-6}T^5$ [M=F$_2$, Ar]	$3.83\times10^{-3}T^{4.5}$ [M=F$_2$, Ar]
Collisional relaxation of HF by He	HF(1)+He→HF(0)+He	$1.54\times10^{-6}T^5$	$3.70\times10^{-5}T^{4.5}$
	HF(2)+He→HF(1)+He	$3.08\times10^{-6}T^5$	$2.41\times10^{-4}T^{4.5}$
	HF(3)+He→HF(2)+He	$4.62\times10^{-6}T^5$	$7.18\times10^{-4}T^{4.5}$
	HF(4)+He→HF(3)+He	$6.16\times10^{-6}T^5$	$1.56\times10^{-3}T^{4.5}$
	HF(5)+He→HF(4)+He	$7.70\times10^{-6}T^5$	$2.85\times10^{-3}T^{4.5}$
	HF(6)+He→HF(5)+He	$9.24\times10^{-6}T^5$	$4.67\times10^{-3}T^{4.5}$
	HF(7)+He→HF(6)+He	$1.08\times10^{-6}T^5$	$7.08\times10^{-3}T^{4.5}$
Collisional relaxation of HF by F atoms	HF(1)+F→HF(0)+F	$1.6\times10^{13}e^{-2.7/RT}$	$1.60\times10^{13}e^{-2.7/RT}$
	HF(2)+F→HF(1)+F	$3.2\times10^{13}e^{-2.7/RT}$	$1.04\times10^{14}e^{-2.7/RT}$
	HF(3)+F→HF(2)+F	$4.8\times10^{13}e^{-2.7/RT}$	$3.11\times10^{14}e^{-2.7/RT}$
	HF(4)+F→HF(3)+F	$6.4\times10^{13}e^{-2.7/RT}$	$6.76\times10^{14}e^{-2.7/RT}$
	HF(5)+F→HF(4)+F	$8.0\times10^{13}e^{-2.7/RT}$	$1.23\times10^{15}e^{-2.7/RT}$
	HF(6)+F→HF(5)+F	$9.6\times10^{13}e^{-2.7/RT}$	$2.02\times10^{15}e^{-2.7/RT}$
	HF(7)+F→HF(6)+F	$1.12\times10^{14}e^{-2.7/RT}$	0

[a]Units: cm^{3}mole^{-1} s^{-1}; kcal mol^{-1}.
[b]Cohen and Bott (Ref. 1).
[c]Cohen and Bott (Ref. 3).
[d]Deactivation of $v=7$ and 8 was unintentionally neglected in the original 1982 Cohen and Bott compilation (Ref. 3).

cantly different product vibrational distributions. The reaction of atomic hydrogen with molecular fluorine (often referred to as the ''hot'' HF generation reaction) produces highly vibrationally excited HF while F+H$_2$ (the ''cold'' HF generation reaction) produces only moderate vibrational excitation, see below. The vibrational distribution for H+F$_2$ peaks at $v=6$ and extends up to $v=9$. Table 5 summarizes the vibrational distributions recommended by the Cohen and Bott[1-4] reviews as well as the measured distributions from a variety of experiments. Most experimental measurements, particularly those of Polanyi,[17] Jonathan,[18] and Tardy,[19] analyzed their data using Einstein coefficients that have since been shown to be inaccurate.[8,20,21] Hence, corrected distributions using the recommended set of A coefficients[9] are shown in parentheses in Table 5.

In general, the available experimental results are in reasonable agreement for the HF(v) distribution. The only uncertainty concerns the nascent population of $v\geq8$. On the low end, the fast flow reactor studies of Setser[22] and Kaufman[23] found no P_8-P_{10}, while on the high end the pressure–pulse chemiluminescence mapping experiments of Tardy[19] found substantial populations for $v=8-9$. The presence of at least some P_8-P_{10} is supported by the infrared

chemiluminescence studies of Polanyi and Jonathan, who reported minor P_8-P_{10}. The nascent vibrational populations from recent theoretical calculations[24] are in satisfactory agreement with experiment but have slightly narrower distributions with small but nonzero population of $v=8-10$.

Surprisingly, the Cohen and Bott reviews recommend no initial population of $v=0-2$, even though all of the experimental measurements (most of which were available at the time) indicate small, but nonzero P_1 and P_2. Clearly, some initial population of $v=1-2$ is indicated by the experimental evidence, and in light of this, we recommend the distribution given in the final column of Table 5. This distribution attempts to encompass the general observation that $v=8-9$ is present but at lower populations than suggested by Tardy. The recommended values for $v=1-6$ are simply the average and one standard deviation from the five experimental measurements. Recommendations for $v=0$, $v=7-10$ are estimates based on the experimental values and have significantly larger error bars ($\pm50\%$ or more). Our distribution is similar in shape to the DF(v) distribution generated by the D+F$_2$ reaction,[19,25] which falls off rapidly beyond the peak at $v=9-10$.

Surprisingly, the total rate constant for H+F$_2$ has not been

TABLE 4. HF rate package comparison—room temperature rate constants

Category	Reaction	Rate constant[a]	
		Cohen and Bott[2,b]	Cohen and Bott[3,c,d]
HF generation	$F+H_2(0)\rightarrow HF(1)+H$	3.084×10^{-12}	4.031×10^{-12}
	$F+H_2(0)\rightarrow HF(2)+H$	9.967×10^{-12}	1.478×10^{-11}
	$F+H_2(0)\rightarrow HF(3)+H$	5.080×10^{-12}	8.063×10^{-12}
	$H+F_2\rightarrow HF(3)+F$	2.844×10^{-13}	1.082×10^{-13}
	$H+F_2\rightarrow HF(4)+F$	4.622×10^{-13}	2.009×10^{-13}
	$H+F_2\rightarrow HF(5)+F$	1.244×10^{-12}	3.555×10^{-13}
	$H+F_2\rightarrow HF(6)+F$	1.564×10^{-12}	5.100×10^{-13}
	$H+F_2\rightarrow HF(7)+F$	0	2.318×10^{-13}
	$H+F_2\rightarrow HF(8)+F$	0	1.855×10^{-13}
Reactive quenching	$H+HF(3)\rightarrow H_2(0)+F$	6.261×10^{-12}	2.153×10^{-11}
	$H+HF(4)\rightarrow H_2(0)+F$	6.524×10^{-13}	2.153×10^{-11}
	$H+HF(5)\rightarrow H_2(0)+F$	2.795×10^{-12}	2.153×10^{-11}
	$H+HF(6)\rightarrow H_2(0)+F$	2.623×10^{-12}	2.153×10^{-11}
	$H+HF(4)\rightarrow H_2(1)+F$	6.524×10^{-13}	2.153×10^{-11}
	$H+HF(5)\rightarrow H_2(1)+F$	4.969×10^{-12}	4.307×10^{-11}
	$H+HF(6)\rightarrow H_2(1)+F$	2.623×10^{-12}	2.153×10^{-11}
	$H+HF(6)\rightarrow H_2(2)+F$	6.653×10^{-12}	6.460×10^{-11}
Self relaxation of HF (quenching by ground state HF)	$HF(1)+HF\rightarrow HF(0)+HF$	1.656×10^{-12}	1.656×10^{-12}
	$HF(2)+HF\rightarrow HF(1)+HF$	6.624×10^{-12}	1.004×10^{-11}
	$HF(3)+HF\rightarrow HF(2)+HF$	9.936×10^{-12}	2.881×10^{-11}
	$HF(4)+HF\rightarrow HF(3)+HF$	4.968×10^{-12}	6.094×10^{-11}
	$HF(5)+HF\rightarrow HF(4)+HF$	1.656×10^{-11}	1.088×10^{-10}
	$HF(6)+HF\rightarrow HF(5)+HF$	2.318×10^{-11}	1.747×10^{-10}
	$HF(2)+HF\rightarrow HF(0)+HF$	3.312×10^{-12}	0
	$HF(3)+HF\rightarrow HF(1)+HF$	2.484×10^{-12}	0
	$HF(4)+HF\rightarrow HF(2)+HF$	4.968×10^{-12}	0
	$HF(5)+HF\rightarrow HF(3)+HF$	8.280×10^{-12}	0
	$HF(6)+HF\rightarrow HF(4)+HF$	1.159×10^{-11}	0
	$HF(3)+HF\rightarrow HF(0)+HF$	2.484×10^{-12}	0
	$HF(4)+HF\rightarrow HF(1)+HF$	4.968×10^{-12}	0
	$HF(5)+HF\rightarrow HF(2)+HF$	8.280×10^{-12}	0
	$HF(6)+HF\rightarrow HF(3)+HF$	1.159×10^{-11}	0
	$HF(4)+HF\rightarrow HF(0)+HF$	4.968×10^{-12}	0
	$HF(5)+HF\rightarrow HF(1)+HF$	8.280×10^{-12}	0
	$HF(6)+HF\rightarrow HF(2)+HF$	1.159×10^{-11}	0
	$HF(5)+HF\rightarrow HF(0)+HF$	8.280×10^{-12}	0
	$HF(6)+HF\rightarrow HF(1)+HF$	1.159×10^{-11}	0
	$HF(6)+HF\rightarrow HF(0)+HF$	1.159×10^{-11}	0
HF V–V energy transfer	$HF(1)+HF(1)\rightarrow HF(2)+HF(0)$	1.993×10^{-11}	2.541×10^{-11}
	$HF(2)+HF(2)\rightarrow HF(3)+HF(1)$	8.303×10^{-12}	2.275×10^{-11}
	$HF(3)+HF(3)\rightarrow HF(4)+HF(2)$	5.535×10^{-12}	2.519×10^{-11}
	$HF(4)+HF(4)\rightarrow HF(5)+HF(3)$	4.151×10^{-12}	2.723×10^{-11}
	$HF(5)+HF(5)\rightarrow HF(6)+HF(4)$	3.321×10^{-12}	2.900×10^{-11}
	$HF(6)+HF(6)\rightarrow HF(7)+HF(5)$	2.768×10^{-12}	3.061×10^{-11}
	$HF(1)+HF(2)\rightarrow HF(0)+HF(3)$	9.963×10^{-12}	2.928×10^{-11}
	$HF(1)+HF(3)\rightarrow HF(0)+HF(4)$	6.642×10^{-12}	3.238×10^{-11}
	$HF(1)+HF(4)\rightarrow HF(0)+HF(5)$	4.982×10^{-12}	3.498×10^{-11}
	$HF(1)+HF(5)\rightarrow HF(0)+HF(6)$	3.985×10^{-12}	3.731×10^{-11}
	$HF(1)+HF(6)\rightarrow HF(0)+HF(7)$	3.321×10^{-12}	3.936×10^{-11}
	$HF(2)+HF(3)\rightarrow HF(1)+HF(4)$	5.535×10^{-12}	2.519×10^{-11}
	$HF(2)+HF(4)\rightarrow HF(1)+HF(5)$	4.151×10^{-12}	2.723×10^{-11}
	$HF(2)+HF(5)\rightarrow HF(1)+HF(6)$	3.321×10^{-12}	2.900×10^{-11}
	$HF(2)+HF(6)\rightarrow HF(1)+HF(7)$	2.768×10^{-12}	3.061×10^{-11}
	$HF(3)+HF(4)\rightarrow HF(2)+HF(5)$	4.151×10^{-12}	2.723×10^{-11}
	$HF(3)+HF(5)\rightarrow HF(2)+HF(6)$	3.321×10^{-12}	2.900×10^{-11}
	$HF(3)+HF(6)\rightarrow HF(2)+HF(7)$	2.768×10^{-12}	3.061×10^{-11}
	$HF(4)+HF(5)\rightarrow HF(3)+HF(6)$	3.321×10^{-12}	2.900×10^{-11}
	$HF(4)+HF(6)\rightarrow HF(3)+HF(7)$	2.768×10^{-12}	3.061×10^{-11}
	$HF(5)+HF(6)\rightarrow HF(4)+HF(7)$	3.321×10^{-12}	3.061×10^{-11}

TABLE 4. HF rate package comparison—room temperature rate constants—Continued

Category	Reaction	Rate constant[a]	
		Cohen and Bott[2,b]	Cohen and Bott[3,c,d]
	$HF(0)+H_2(1)\rightarrow HF(1)+H_2(0)$	1.328×10^{-12}	1.366×10^{-12}
	$HF(1)+H_2(1)\rightarrow HF(2)+H_2(0)$	2.657×10^{-12}	1.742×10^{-12}
	$HF(2)+H_2(1)\rightarrow HF(3)+H_2(0)$	3.985×10^{-12}	2.010×10^{-12}
	$HF(3)+H_2(1)\rightarrow HF(4)+H_2(0)$	5.314×10^{-12}	2.220×10^{-12}
	$HF(4)+H_2(1)\rightarrow HF(5)+H_2(0)$	6.642×10^{-12}	2.402×10^{-12}
	$HF(5)+H_2(1)\rightarrow HF(6)+H_2(0)$	7.971×10^{-12}	2.556×10^{-12}
	$HF(0)+H_2(2)\rightarrow HF(1)+H_2(1)$	1.328×10^{-12}	0
	$HF(1)+H_2(2)\rightarrow HF(2)+H_2(1)$	2.657×10^{-12}	0
	$HF(2)+H_2(2)\rightarrow HF(3)+H_2(1)$	3.985×10^{-12}	0
Vibrational	$HF(3)+H_2(2)\rightarrow HF(4)+H_2(1)$	5.314×10^{-12}	0
energy transfer	$HF(4)+H_2(2)\rightarrow HF(5)+H_2(1)$	6.642×10^{-12}	0
from $H_2(1-3)$	$HF(5)+H_2(2)\rightarrow HF(6)+H_2(1)$	7.971×10^{-12}	0
	$HF(0)+H_2(2)\rightarrow HF(2)+H_2(0)$	2.657×10^{-12}	0
	$HF(1)+H_2(2)\rightarrow HF(3)+H_2(0)$	3.985×10^{-12}	0
	$HF(2)+H_2(2)\rightarrow HF(4)+H_2(0)$	5.314×10^{-12}	0
	$HF(3)+H_2(2)\rightarrow HF(5)+H_2(0)$	6.642×10^{-12}	0
	$HF(4)+H_2(2)\rightarrow HF(6)+H_2(0)$	7.971×10^{-12}	0
	$HF(0)+H_2(3)\rightarrow HF(3)+H_2(0)$	3.985×10^{-12}	0
	$HF(1)+H_2(3)\rightarrow HF(4)+H_2(0)$	5.314×10^{-12}	0
	$HF(2)+H_2(3)\rightarrow HF(5)+H_2(0)$	6.642×10^{-12}	0
	$HF(3)+H_2(3)\rightarrow HF(6)+H_2(0)$	7.971×10^{-12}	0
	$HF(1)+H_2\rightarrow HF(0)+H_2$	2.989×10^{-14}	1.070×10^{-14}
Collisional	$HF(2)+H_2\rightarrow HF(1)+H_2$	5.978×10^{-14}	6.956×10^{-14}
relaxation	$HF(3)+H_2\rightarrow HF(2)+H_2$	8.967×10^{-14}	2.076×10^{-13}
of HF	$HF(4)+H_2\rightarrow HF(3)+H_2$	1.196×10^{-13}	4.516×10^{-13}
by H_2	$HF(5)+H_2\rightarrow HF(4)+H_2$	1.495×10^{-13}	8.251×10^{-13}
	$HF(6)+H_2\rightarrow HF(5)+H_2$	1.793×10^{-13}	1.351×10^{-12}
	$HF(7)+H_2\rightarrow HF(6)+H_2$	2.092×10^{-13}	0
	$HF(1)+H\rightarrow HF(0)+H$	7.698×10^{-13}	2.053×10^{-13}
	$HF(2)+H\rightarrow HF(1)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(3)+H\rightarrow HF(2)+H$	2.771×10^{-10}	7.749×10^{-11}
	$HF(4)+H\rightarrow HF(3)+H$	2.771×10^{-10}	1.107×10^{-10}
	$HF(5)+H\rightarrow HF(4)+H$	2.771×10^{-10}	1.495×10^{-10}
	$HF(6)+H\rightarrow HF(5)+H$	2.771×10^{-10}	1.937×10^{-10}
	$HF(7)+H\rightarrow HF(6)+H$	0	3.592×10^{-13}
	$HF(2)+H\rightarrow HF(0)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(3)+H\rightarrow HF(1)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(4)+H\rightarrow HF(2)+H$	1.386×10^{-12}	3.592×10^{-13}
Collisional	$HF(5)+H\rightarrow HF(3)+H$	1.386×10^{-12}	3.592×10^{-13}
relaxation	$HF(6)+H\rightarrow HF(4)+H$	1.386×10^{-12}	3.592×10^{-13}
of HF	$HF(7)+H\rightarrow HF(5)+H$	1.386×10^{-12}	3.592×10^{-13}
by H atoms	$HF(3)+H\rightarrow HF(0)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(4)+H\rightarrow HF(1)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(5)+H\rightarrow HF(2)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(7)+H\rightarrow HF(4)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(4)+H\rightarrow HF(0)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(5)+H\rightarrow HF(1)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(6)+H\rightarrow HF(2)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(5)+H\rightarrow HF(0)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(6)+H\rightarrow HF(1)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(6)+H\rightarrow HF(0)+H$	1.386×10^{-12}	3.592×10^{-13}
	$HF(1)+M\rightarrow HF(0)+M$	3.107×10^{-18}	4.659×10^{-18}
Collisional	$HF(2)+M\rightarrow HF(1)+M$	6.214×10^{-18}	3.029×10^{-17}
relaxation	$HF(3)+M\rightarrow HF(2)+M$	9.321×10^{-18}	9.039×10^{-17}
of HF	$HF(4)+M\rightarrow HF(3)+M$	1.243×10^{-17}	1.966×10^{-16}
by M	$HF(5)+M\rightarrow HF(4)+M$	1.554×10^{-17}	3.588×10^{-16}
	$HF(6)+M\rightarrow HF(5)+M$	1.864×10^{-17}	5.871×10^{-16}
	$HF(7)+M\rightarrow HF(6)+M$	2.175×10^{-17}	8.923×10^{-16}

TABLE 4. HF rate package comparison—room temperature rate constants—Continued

Category	Reaction	Rate constant[a]	
		Cohen and Bott[2,b]	Cohen and Bott[3,c,d]
Collisional relaxation of HF by He	$HF(1)+He \rightarrow HF(0)+He$	6.214×10^{-18}	8.620×10^{-18}
	$HF(2)+He \rightarrow HF(1)+He$	1.243×10^{-17}	5.615×10^{-17}
	$HF(3)+He \rightarrow HF(2)+He$	1.864×10^{-17}	1.673×10^{-16}
	$HF(4)+He \rightarrow HF(3)+He$	2.486×10^{-17}	3.634×10^{-16}
	$HF(5)+He \rightarrow HF(4)+He$	3.107×10^{-17}	6.640×10^{-16}
	$HF(6)+He \rightarrow HF(5)+He$	3.729×10^{-17}	1.088×10^{-15}
	$HF(7)+He \rightarrow HF(6)+He$	4.358×10^{-17}	1.649×10^{-15}
Collisional relaxation of HF by F atoms	$HF(1)+F \rightarrow HF(0)+F$	2.866×10^{-13}	2.866×10^{-13}
	$HF(2)+F \rightarrow HF(1)+F$	5.732×10^{-13}	1.863×10^{-12}
	$HF(3)+F \rightarrow HF(2)+F$	8.598×10^{-13}	5.571×10^{-12}
	$HF(4)+F \rightarrow HF(3)+F$	1.146×10^{-12}	1.211×10^{-11}
	$HF(5)+F \rightarrow HF(4)+F$	1.433×10^{-12}	2.203×10^{-11}
	$HF(6)+F \rightarrow HF(5)+F$	1.720×10^{-12}	3.618×10^{-11}
	$HF(7)+F \rightarrow HF(6)+F$	2.006×10^{-12}	0

[a]Units: cm^3 molecule^{-1} s^{-1}.
[b]See Cohen and Bott (Ref. 1).
[c]See Cohen and Bott (Ref. 3).
[d]Deactivation of $v=7$ and 8 was unintentionally neglected in the original 1982 Cohen and Bott review (Ref. 3).

TABLE 5. Experimentally determined nascent vibrational distributions for $H+F_2$

v	CFD kinetics packages		Experimental measurements[a]					Recommended[d]
	Ref. 2	Ref. 3	Ref. 18[b]	Ref. 17[b]	Ref. 19[c]	Ref. 22	Ref. 23	
0	0.00	0.00	<0.04 (<0.03)	≤0.10 (0.08)	0.00 (0.00)	0.00	0.00	0.04±0.04
1	0.00	0.00	0.09 (0.06)	0.12 (0.07)	0.15 (0.14)	0.07	0.06	0.08±0.03
2	0.00	0.00	0.11 (0.08)	0.13 (0.10)	0.13 (0.12)	0.17	0.12	0.13±0.03
3	0.18	0.21	0.13 (0.10)	0.25 (0.20)	0.27 (0.26)	0.28	0.17	0.20±0.07
4	0.30	0.39	0.45 (0.36)	0.35 (0.30)	0.41 (0.40)	0.59	0.37	0.40±0.11
5	0.80	0.70	0.89 (0.83)	0.78 (0.70)	0.72 (0.70)	0.93	0.76	0.78±0.10
6	1.00	1.00	1.00 (1.00)	1.00 (1.00)	1.00 (1.00)	1.00	1.00	1.00
7	0.00	0.45	0.45 (0.43)	0.40 (0.48)	0.76 (0.80)	0.52	0.62	0.50±0.25
8	0.00	0.36	0.20 (0.19)	0.26 (0.37)	0.46 (0.49)	0.00	0.00	0.30±0.15
9	0.00	0.00	<0.04 (<0.01)	0.16 (0.12)	0.41 (0.43)	0.00	0.00	0.15±0.15
10	0.00	0.00	<0.04 (<0.01)	0.00 (0.00)	0.00 (0.00)	0.00	0.00	0.01±0.01

[a]The values in parentheses for Jonathan, Polanyi, and Tardy are corrected for the Einstein coefficients of Setser (Ref. 9).
[b]The corrected values shown were calculated from the distributions reported by Kaufman (Ref. 23) which were corrected for the Einstein coefficients of Sileo and Cool (Ref. 10).
[c]Tardy (Ref. 19) originally used the Einstein coefficients of Meredith and Smith (Ref. 20).
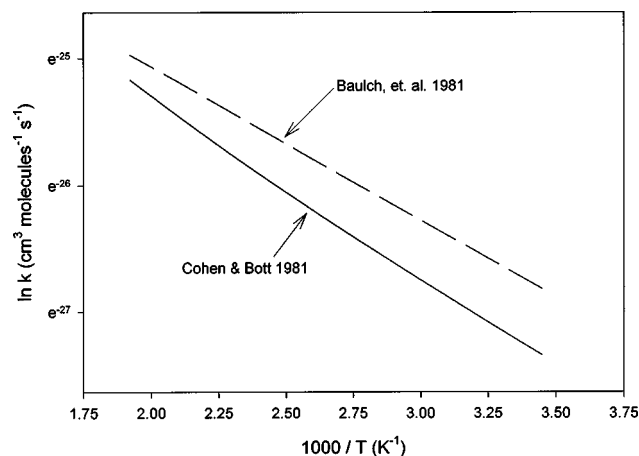[d]See text for details.

FIG. 1. Comparison of $H+F_2$ Arrhenius expressions. The recommended rate constant expression of Baulch *et al.* (Ref. 28) is compared with the recommended expression of Cohen and Bott (Ref. 4). The Baulch expression results in consistently higher values for the rate constant. The difference is ~40% at room temperature but reduces to ~20% at 500 K.

FIG. 2. Comparison of $F+H_2$ Arrhenius expressions. The recommended rate constant expression for the 190–376 K range (Persky and Kornweitz) (Ref. 34) is compared with the expression of Heidner and co-workers (Ref. 38) which measured $k(F+H_2)$ for $T = 295–765$ K. Broken lines show extrapolations from the recommended ranges.

firmly established. The 1982 Cohen and Bott review[3] gives $k(T) = 5.0 \times 10^{-15} T^{1.5} \exp(-845/T)$ cm^3 molecules^{-1} s^{-1} and the 1983 Cohen and Westberg recommendation[4] is essentially the same, $4.8 \times 10^{-15} T^{1.4} \exp(-667/T)$ cm^3 molecules^{-1} s^{-1}. In both cases, the recommended value was based on the experiments of Homann and co-workers[26] and unpublished transition state theory calculations of Westberg and Cohen.[27] The 1981 Baulch kinetic[28] database recommends $k = 1.46 \times 10^{-10} \exp(-1210/T)$ cm^3 molecules^{-1} s^{-1} for $T = 290–570$ K and points out that Homann's result is significantly smaller (approximately a factor of 2 at 300 K) than previous results by Rabideau,[29] Vasil'ev,[30] and Goldberg.[31] The Cohen and Bott[3] and Baulch[28] expressions are compared in Fig. 1. At room temperature, they differ by ~40%, while at 500 K, the difference is reduced to ~20%. In lieu of more information, we adopt the 1982 Cohen and Bott recommendation.[3] A new measurement of the total H atom removal rate constant and the nascent HF distribution would be particularly useful.

2.2.1.2. $F+H_2$

The $F+H_2$ reaction is a prototypical system for fundamental reaction dynamics, and as such, has been a favorite subject for both theoretical and experimental state-to-state reactive scattering studies. The reaction is particularly amenable to molecular beam studies and vibrationally state resolved differential cross sections have been measured.[32] Corresponding high level *ab initio* calculations and simulations[33] have achieved very good agreement with experiment. The vibrational distribution remains unchanged from the 1982 Cohen and Bott report,[3] 0.00 : 0.15 : 0.55 : 0.30 for $v = 0–3$.

A recent review by Persky and Kornweitz[34] has refined the overall rate constant for the $F+H_2$ reaction. Following a detailed examination of relevant publications they recommend $k(T) = (1.1 \pm 0.1) \times 10^{-10} \exp(-(450 \pm 50)/T)$
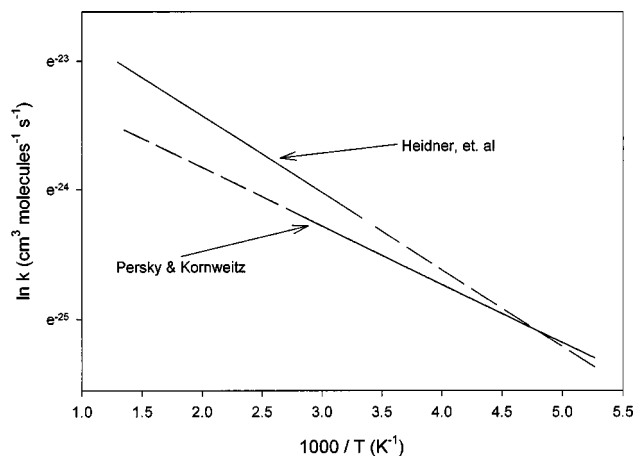
cm^3 molecules^{-1} s^{-1} over the 190 K–376 K temperature range, and $(2.43 \pm 0.15) \times 10^{-11}$ cm^3 molecules^{-1} s^{-1} at 298 K. This compares reasonably well with literature reviews published in 1983[4] $(k(T) = 4.5 \times 10^{-12} T^{0.5} \exp(-319/T)$ and $k_{298} = 2.66 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}), 1992[35] and 1997[36] $(k(T) = 1.4 \times 10^{-10} \exp(-(500 \pm 200)/T)$ and $k_{298} = (2.6 \pm 0.6) \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}), as well as the Cohen and Bott reviews of 1977[2] $(k(T) = 2.7 \times 10^{-10} \exp(-805/T)$ and $k_{298} = 1.8 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}) and 1982[3] $(k(T) = 4.32 \times 10^{-12} T^{0.5} \exp(-307/T)$ and $k_{298} = 2.7 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}). The most recent review by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry[37] adopted the Persky recommendation.[34] Unfortunately, the limited temperature range of the Persky expression is problematic for HF laser modeling, since the laser typically operates at substantially higher temperatures. To date, there has been only one experiment that has measured $k(F+H_2)$ above 376 K. Heidner and co-workers[38] monitored the time-resolved infrared emission of product HF following multiphoton dissociation of SF$_6$ in the presence of H$_2$ over the 295–765 K temperature range. The resulting Arrhenius expression for $k(F+H_2)$ is $(2.2 \pm 0.4) \times 10^{-10} \exp(-(595 \pm 50)/T)$ cm^3 molecules^{-1} s^{-1}, just 7% smaller than Persky's at room temperature but 40% larger if Persky's expression is extrapolated to 765 K, see Fig. 2. Persky and Kornweitz[34] considered Heidner's results ''problematic with regard to the calculated kinetic isotope effect.'' Indeed, the Heidner experiment gave a temperature independent kinetic isotope effect while the accepted value is

$$\frac{k_{F+H_2}}{k_{F+D_2}} = (1.04 \pm 0.02) \exp((186 \pm 5)/T). \quad (6)$$

In lieu of more data for $T > 376$, we recommend the conclusions of Persky and Kornweitz[34] for the 190–376 K temperature range and the expression of Heidner and co-workers[38] for $T > 376$ K.

Some CFD codes[5] include F atom reactions with vibrationally excited H_2 even though this process was not included in the original Cohen and Bott compilations. There have been no specific experimental measurements to support or refute this assumption and we do not recommend inclusion of reactive processes that involve vibrationally hot H_2. In any case, it is unlikely that inclusion of these reactions will have any effect on the overall performance of the laser because $[H_2(v>0)]$ should be extremely small.

2.2.2. Reactive Quenching

Vibrationally excited HF can be removed by hydrogen atoms by $V-R,T$ inelastic collisions (see Sec. 2.2.5.1 below) or by chemical reaction to give molecular hydrogen and an F atom:

$$H + HF(v) \rightarrow H_2 + F. \tag{7}$$

In principle, microreversibility enables one to calculate the rate constant for Eq. (7) from the extensive data available for the well-studied $F+H_2$ reaction. In fact, numerous theoretical studies have attempted to do this using the $F+H_2$ potential energy surface.[39] According to these calculations the barrier to F atom transfer is large, ~ 33 kcal mol^{-1}, and reaction (7) should be slow for $v<3$.[40] This is consistent with the experimental results of Heidner and co-workers[41,42] who measured HF(v) deactivation by H atoms directly using HF laser induced fluorescence, and the flow tube measurements of Kwok and Wilkins.[43] These experiments report a large change in the HF(v) removal rate constant for $v=1-2$ versus 3. This change is generally attributed to the opening of the reactive channel for $v\geqslant3$. However, according to Heidner[42] only a fraction of the total H+HF(3) encounters that result in removal of HF(3) proceed via chemical reaction and the upper limit for reactive quenching, $k(H+HF(3)\rightarrow H_2+F)$, is 5.0×10^{-11} cm^3 molecules^{-1} s^{-1}.

The 1981 Baulch kinetics database[28] makes no recommendation for k_7 because the experimental evidence available at the time was inconsistent with the data for the well established forward reaction, $F+H_2$. While there have been no new experiments (for thermal collisions) since the work of Heidner and Bott,[41,42] the available theoretical calculations support their slower reaction rate constants.[1,44]

2.2.3. HF Self-Relaxation and $V-V$ Energy Transfer

2.2.3.1. Self-Relaxation
#### (Deactivation by Ground State HF)

One of the most active areas of HF kinetics research in the past 15 years has been in the study of HF self-relaxation and vibrational energy transfer. The importance of these processes is acute for obvious reasons. Unfortunately, a consensus regarding the magnitude of the rate constants had not been reached prior to 1982. For example, the 1977 Cohen and Bott[1] compilation contain moderate to large rate constants for single- and multiquantum $V-R,T$ deactivation of HF by ground state HF

$$HF(v) + HF \rightarrow HF(v') + HF, \tag{8}$$
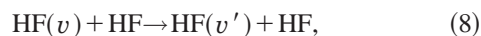
while the 1982 Cohen and Bott package[3] includes only single-quantum deactivations. Significant differences also exist for the HF $V-V$ energy transfer reactions such as

$$HF(v) + HF(0) \rightarrow HF(v-1) + HF(1). \tag{9}$$
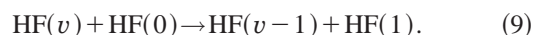
Implicitly included in reaction (8) are the $V-R$ redistribution processes that produce highly rotationally excited HF:

$$HF(v,J) + HF \rightarrow HF(v-1,J'\geqslant10) + HF. \tag{10}$$
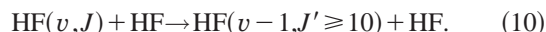
As will be discussed in detail in Sec. 2.4. below, this quenching process is of special interest because it has the potential to contribute significantly to rotational nonequilibrium.

Shortly after the publication of the 1982 review,[3] the Crim group at the University of Wisconsin[45–49] and the Kaufman group at the University of Pittsburgh[23,50–52] undertook a major effort to characterize the total self-relaxation rate constants and the mechanism for HF self-relaxation. Crim's group used a double resonance type of experiment where the vibrationally excited HF molecules were prepared in discrete rovibrational states by a pulsed laser. The time resolved fluorescence and/or $\Delta v=1$ absorption signals were analyzed to determine total quenching rates and relaxation mechanisms. Kaufman prepared vibrationally excited HF in a flow reactor where dilute flows of H or F atoms (generated by a microwave discharge) were reacted with a variety of F or H atom donors. The infrared emission was collected with an InSb detector and circularly variable filter. A modified Stern–Volmer analysis was applied to the quenching data. Table 6 compares the experimentally determined rate constants for HF self-relaxation with a variety of other experiments,[53–63] relevant calculations,[64–66] and the standard kinetics packages.[1–4] The agreement for $v=1-7$ is, in general, excellent and k_8 is well established. The experimental relaxation rates scale as $v^{2.9}$ and are independent of the initial rotational quantum number.

In addition to total quenching rate constants, the Crim and Kaufman laboratories also determined the relaxation mechanism. Kaufman's group argued strongly for a $V-T,R$ mechanism (rather than $V-V$ energy transfer) based on Lambert-Salter plots[52] and the magnitude of the rate constants. In particular, they pointed out that if the predominant mechanism were $V-V$ energy transfer, (e.g., HF(7)+HF(0)→HF(6)+HF(1)) then the rate constant for the exothermic reverse process would be 100 times greater than the gas kinetic limit. Crim's double resonance experiments were able to quantify the role of $V-V$ energy transfer. They found that the fraction of inelastic HF(v)+HF(0) room temperature encounters that proceed via $V-T,R$ relaxation, is 1.0 (0.41±0.10), (0.56±0.05), (0.84±0.05), and (0.98 ±0.19) for $v=1-5$, respectively.[49,47] For $v>3$, vibrational energy transfer to the ground state collision partner plays a relatively minor role in the relaxation process. Both Crim and Kaufman agree that multiquantum relaxation is unimportant,[49,52] even though work by Pimentel and Thompson (see Sec. 2.4 below) suggested the possibility of multi-

TABLE 6. HF total self relaxation rate constants

Reference	$k_{300}(HF(v)+HF)\rightarrow$ products, $(10^{-12}$ cm^3 molecules^{-1} s$^{-1})$						
	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$	$v=6$	$v=7$
Experiments							
Bott and Cohen[56]	1.8±0.3						
Hinchen and Hobbs[54]	1.8±0.2						
Bina and Jones[55]	2.3±0.3	5±2					
Kwok and Wilkins[57]	1.6±0.6	16±5	26±9	27±10	(58)[a]	(101)[a]	
Osgood et al.[61]	1.7	25±7	49±15	43±18			
Airey and Smith[58]		16	17	⩾44	⩾65		
Poole and Smith[59,60]		13	19	32	46	52	~43
Douglas and Moore[62]			28±4	72±5			
Lampert et al.[63]			32±6	88±11			
Dzelzkalns and Kaufman[23,50–52]	1.8	19	31	73	140	290	450
Copeland et al.[45]	1.46±0.1	19.8±1.0					
Jursich and Crim[49]			30.2±3.0	72.8±2.7	151±8		
Calculations							
Wilkins and Kwok[64]	1.7	22	29	33	42	51	
Coltrin and Marcus[65]	0.2±0.1	19±3	28±4	53±10	69±10	156±11	455±49
Billing and Poulsen[66]	0.81	6.2±2.2	10±4	19±7	27±10	43±15	82±29
Standard Kinetics Packages[b]							
Cohen and Bott 1977[2]	1.66	6.62	9.94	4.97	16.6	23.2	82.8
Cohen and Bott 1982[3]	1.66	10.0	28.8	60.9	108.8	174.7	260.9

[a]M. A. Kwok and N. Cohen, personal communication reported in Ref. 50.
[b]Only single quantum deactivation rate constants are listed.

quantum $V-R$ transfer with Δv as large as 5. Crim probed the role of multiquantum deactivations directly and found that 0.98 ± 0.19 and (0.87 ± 0.21) of the relaxed HF(4) and HF(5) molecules, respectively, appear in the next lower vibrational level.[49] It is important to note that Crim and co-workers' results are based on the assumption that $V-T,R$ processes that produce metastable high rotational states (which would not be detected in their experiment) can be neglected. The invariance of the vibrational relaxation rate constant with initial rotational quantum number and the work of Leone (see Sec. 2.4 below) tend to validate this assumption.

Finally, Crim and co-workers found that the rate constants for HF self-relaxation are inversely dependent on temperature,[46,48] see Table 7 and Fig. 3. Crim and co-workers interpret their temperature dependent data in terms of relaxation probabilities. The functional form of the fitting function suggests that long-range forces dominate the relaxation process:

$$P_v(T)=AT^{-m}, \quad (11)$$

where $P_v=k_v/k_c$ (k_c is the gas kinetic rate constant for a collision diameter of 0.25 nm) and A and m are fitting parameters. Sample fits of Crim's tabulated relaxation probabilities are shown in Fig. 3. Strangely, the A values determined by our fits (where $m=1.3$ was fixed) vary significantly from Crim's analysis:[48] A(Crim)= 22, 370, 880, and 1850 for $v=1$, 3, 4, and 5, respectively, while A(thiswork)= 12, 315, 764, and 1610 for the same v levels. Nonetheless, considering the overall agreement in the literature for $v=1-7$ and the accuracy of double resonance tech-

nique, we recommend the HF self-quenching rate constants listed in Table 7. The temperature dependence of $v\geq6$ has not been measured. If the temperature dependence found for $v=1-5$ (i.e., $k_v=P_v^*k_c=k_c^*A^*T^{-1.3}$) is applied, then $A(6)=3107$ and $A(7)=4339$ are calculated from the measured room temperature values.

2.2.3.2. V–V Energy Transfer (Deactivation by HF(v>0))

Besides simple $\Delta v=-1$ relaxation, vibrationally excited, anharmonic diatomic molecules such as HF and CO can have $V-V$ energy transfer with other vibrationally excited molecules (e.g., reaction (12)) in a process originally described by Treanor[67]

$$HF(v)+HF(v')\rightarrow HF(v+1)+HF(v'-1). \quad (12)$$
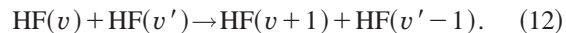
This unusual ability is possible because the spacing between vibrational energy levels decreases with increasing quantum number and reactions like Eq. (12) are slightly exothermic. Unfortunately, it is extremely difficult to measure rate constants for these types of processes. In fact, only measurements for

$$HF(1)+HF(1)\rightarrow HF(2)+HF(0) \quad (12a)$$
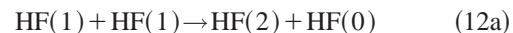
have been reported,[15,57,58,60] $k_{12a}(300\,K)\sim3\times10^{-11}$ cm^3 molecules^{-1} s^{-1}. However, these measurements may include a significant $V-T,R$ contribution and k_{12} is highly uncertain for all vibrational quantum numbers. In lieu of more specific experimental data, the general expression of Cohen and Bott[3] is adopted because of its inclusion of a small, but reasonable v dependence.

TABLE 7. Temperature dependence of $k_v(HF)$[a]

Temperature	$k_v(\times 10^{-12}$ cm^3 molecules^{-1} s^{-1})				
	k_1	k_2	k_3	k_4	k_5
295	1.38 ± 0.09	18.6 ± 0.9	31 ± 2	72 ± 1	149 ± 1
311	1.26 ± 0.03	18.8 ± 0.8			
335					145 ± 5
338	0.98 ± 0.04	17.4 ± 0.6			
350			27 ± 2	70 ± 3	126 ± 11
358	0.88 ± 0.07	18.3 ± 0.7			
383	0.88 ± 0.07	15.7 ± 2.1			
400			22 ± 1	52 ± 5	140 ± 14
413	0.77 ± 0.09	15.8 ± 1.7			
433	0.72 ± 0.03	16.0 ± 1.0			
468	0.63 ± 0.07	17.0 ± 1.4			
470			20.5 ± 2.4	48 ± 3	114 ± 12
493	0.64 ± 0.07	15.1 ± 0.9			
528	0.65 ± 0.04	13.9 ± 0.9			
530			19 ± 2	48 ± 4	93 ± 7
600			20 ± 2	44 ± 2	75 ± 4
605	0.59 ± 0.02	13.3 ± 0.6			
625					81 ± 11
635	0.61 ± 0.07	13.0 ± 1.3			
650			19 ± 2	48 ± 2	
670				46 ± 5	
678	0.77 ± 0.06	14.0 ± 1.6			
718	0.60 ± 0.05	13.3 ± 0.9			

[a]See Refs. 46 and 48.

2.2.4. HF Relaxation and $V-V$ Energy Transfer with H$_2$

There have been several studies of HF(v) relaxation by a variety of molecular quenchers. Table 8 summarizes the results for $Q = H_2$, which are the most relevant to HF laser
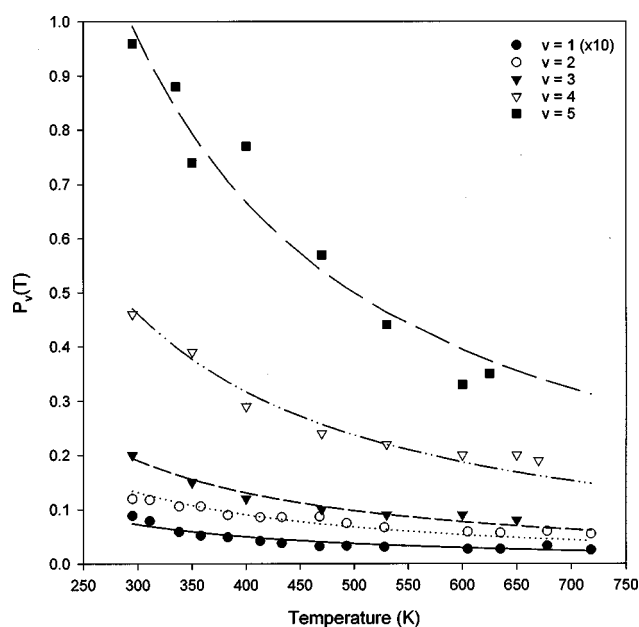

FIG. 3. Self-relaxation probability vs temperature. The tabulated probabilities of relaxation from Refs. 46 and 48 are fit to Eq. (11). The parameter m was fixed to 1.3 while A was optimized. The resulting A parameter values 12.0, 218.0, 315.2, 764.0, 1610.3 for $v = 1-5$, respectively, were determined by least squares fitting.

kinetics.[23,56,59,68–71] With the exception of the work by Poole and Smith,[59] the agreement for the total quenching rate constants is good for $v = 3-5$. The mechanism for the quenching is generally believed to be $V-T,R$ for $v = 3-5$ for two important reasons. First, $V-V$ energy transfer from HF(v) to H$_2$ is endothermic for all single vibrational quantum changes in HF:

$$HF(v) + H_2(0) + \Delta E \geqslant 200 \ cm^{-1} \rightarrow HF(v-1) + H_2(1).$$
(13)
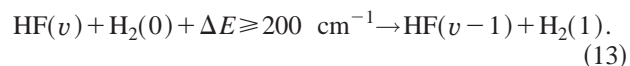
In fact, due to the anhamonicity of HF, the energy gap between HF($\Delta v = -1$) and H$_2$(0-1) increases with vibrational quantum number ($\Delta E_{v-v} = -198$ cm^{-1} for HF(1) and -1171 cm^{-1} for HF(7)). Second, if the endothermic $V-V$ process were the dominant mechanism, then the exothermic reverse process

$$HF(v-1) + H_2(1) \rightarrow HF(v) + H_2(0)$$
(14)

would be several times larger than the gas kinetic limit. Only for HF(1) does a $V-V$ process seem possible, and indeed, vibrational energy transfer is the most likely mechanism for $v = 1$. For $v > 1$, however, the $V-T,R$ process

$$HF(v) + H_2 \rightarrow HF(v-1) + H_2$$
(15)
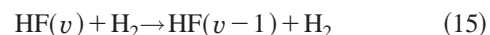
should be the dominant mechanism.

The 1982 Cohen and Bott review[3] contains temperature and vibration dependent expressions for reactions (13) and (15) even though there is no convincing evidence for a temperature dependent quenching process.[69]

TABLE 8. Room temperature rate constants for HF+H$_2$

| Reference | k_{300}(HF(v)+H$_2$→HF)($v-1$)+H$_2$(10^{-12} cm^3 molecules^{-1} s^{-1}) | | | | | | |
	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$	$v=6$	$v=7$
Bott and Cohen[56,68]	0.52±0.03						
Poole and Smith[59]		0.21	0.15	0.21	0.49	0.99	1.6
Douglas and Moore[70]			0.31±0.06	0.47±0.12			
Bott and Heidner[69]	0.52±0.05		0.35±0.04				
Dzelzkalns and Kaufman[23]					1.7±0.5	3.5±1	9.1±2.7
Jursich et al.[71]			0.38±0.25	0.67±0.10	1.64±0.19		
Cohen and Bott[3]	0.01	0.07	0.21	0.45	0.83	1.35	
Recommended	0.52±0.04	0.2±0.1	0.35±0.04	0.50±0.2	1.6±0.3	3.5±1	9.1±2.7

$$k_{13}(\text{Ref.3})=2.4\times10^{10}\nu^{0.35}T^{0.5}e^{(407-\Delta E_v)/RT}\ \text{cm}^3\ \text{mol}^{-1}\text{s}^{-1}, \quad (16)$$

$$k_{15}(\text{Ref.3})=\nu^{2.7}(0.6\times10^{12}T^{-1}+1.0$$
$$\times10^4T^{2.28})\text{cm}^3\ \text{mol}^{-1}\text{s}^{-1}. \quad (17)$$

For example, in 1973 Cohen and Bott measured the temperature dependence[56] ($T=295,450-1000$ K), of HF(1) deactivation by H$_2$ and found that the total deactivation ($k_{13}+k_{15}$) rate was independent of temperature (see Fig. 4 of Ref. 56). A year later Bott remeasured the temperature dependent quenching of HF(1) from 440 K to 690 K and the data showed considerable scatter and only a weak temperature dependence.[68] Finally, in 1980 Bott and Heidner measured HF(1) and HF(3) quenching by H$_2$ at 295 K and 200 K and found deactivation rate coefficients that were constant versus T within their experimental error.[69] Clearly, there is not sufficient evidence to support a T dependent quenching rate constant. Furthermore, the v and T dependent expression for k_{15} significantly underestimates the measured values at room temperature, see Table 8. To the authors' credit, the 1982 package[3] eliminates the energy transfer reactions from H$_2$(2) and H$_2$(3) as well as the $\Delta v>1$ exchanges contained in the 1977 Cohen and Bott package because there is no specific experimental justification for them. We recommend the rate constant values listed in Table 8 for the $V-T,R$ quenching of HF by H$_2$ and assign a T^0 temperature dependence. The HF(v)+H$_2$(v')$V-V$ energy transfer reactions [reaction (14)] are calculated from detailed balance.

2.2.5. HF Vibrational Relaxation by Atomic and Molecular Species

2.2.5.1. H Atoms

In addition to the reactive quenching of HF(v) by H atoms, see Sec. 2.2.2 above, H atoms can vibrationally deactivate HF with rate constants in the 10^{-13} cm^3 molecules^{-1} s^{-1} range for $v=1-2$ and 10^{-10} cm^3 molecules^{-1} s^{-1} range for $v\geqslant3$

$$\text{HF}(v)+\text{H}\rightarrow\text{HF}(v')+\text{H}. \quad (18)$$
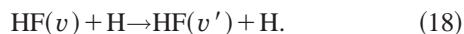
The recommendations in the 1982 Cohen and Bott review are based on the experimental measurements of Bott and

Heidner[41,42] and Polanyi.[72] Besides the experiments and calculations given above for reactive quenching, there have been no new studies of HF quenching by H atoms and the 1982 compilation values are adopted. It is important to note that the pre-exponential factors for $k_{18}(v\geqslant3)$ are calculated by subtracting the contribution of reactive quenching from the measured HF removal rates.[3] While single- and multiquantum deactivations are both possible, the $\Delta v=-1$ processes have the largest rate constants:

$$k_{18}(\Delta\nu=1)=A\times10^{16}T^{-1}\ \text{cm}^3\ \text{mol}^{-1}\text{s}^{-1}, \quad (19a)$$

$$k_{18}(\Delta\nu\geqslant2)=B\times10^{12}e^{(-700/RT)}\ \text{cm}^3\ \text{mol}^{-1}\text{s}^{-1}, \quad (19b)$$

where $A(v=1)=0.4$, $A(v\geqslant2)=0.7$, and $B=1.4$, 2.0, 2.7, and 3.5 for $v=3-6$, respectively. The T^{-1} dependence of the single quantum deactivation rate constant is based on the 295 and 200 K measurements of Bott and Heidner.[42]

2.2.5.2. F Atoms

There have been no new measurements of HF(v) deactivation by F atoms since the 1977 review by Cohen and Bott[2] who based their recommendation on the measurements by Quigley and Wolga,[73] Blauer and Solomon,[74] and Bott and Cohen.[75] Their rate constant expression, which is both v and T dependent, is

$$k(\text{HF}(\nu)+\text{F})=\nu*1.6\times10^{13}\ e^{-2700/RT}. \quad (20)$$

In 1982, Cohen and Bott[3] modified their previous recommendation to add the same $v^{2.7}$ dependence observed for deactivation by HF (see Sec. 2.2.3 above). Unfortunately, there is no specific experimental evidence to support this change and relaxation by H atoms is only moderately v dependent (for $v\geqslant3$). In lieu of experimental evidence for nonlinear v dependence, we recommend the 1977 Cohen and Bott expression.[2]

2.2.5.3. He, Ar, and F$_2$

There have been no new measurements of HF(v) deactivation by He, Ar, or F$_2$ since the 1977 Cohen and Bott review.[2] Their initial recommendation was based on the experimental data of Bott.[76] The measurements were performed in a shock tube at very high temperature ($T>900$ K). The

TABLE 9. Dissociation energy of molecular fluorine

Reference	$D^0(F_2)$ (kcal mol^{-1})
Barrow and Caunt[79]	37.6±3.5
Stamper and Barrow[78]	37.72±0.13
Milne and Gilles[80]	41.3±0.5
Dibeler et al.[81]	30.9±0.7
DeCorpo et al.[82]	37.5±2.3
Blauer and Solomon[83]	37.1±1.2
Colbourn et al.[85]	36.93±0.14
Gole and Margrave[84]	>33.05
JANAF[77]	36.94±0.14

1982 review modified the temperature dependent expressions to include a $v^{2.7}$ dependence. The resulting expression is

$$k_Q(T) = A_Q \times 10^{-5} \, v^{2.7} T^{4.5}, \qquad (21)$$

with $A_Q = 2, 2,$ and 3.7 for Ar, F_2, and He, respectively. However, for the reasons stated above for F atom deactivation of HF(v), we recommend a linear v dependence. Only single quantum deactivations are considered. Considering the lack of data at a variety of temperatures, these values are highly uncertain.

2.3. Fluorine Dissociation and Fluorine Atom Recombination

Although the efficiency of the HF laser depends on many parameters, few are as important as the efficiency of F atom generation, regardless of whether a combustor or electric discharge produces them. The complex interplay of thermal F_2 dissociation, three-body F atom recombination, and heterogeneous (wall) recombination determine the initial [F], and thus the maximum concentration of vibrationally excited HF.

The dissociation energy for molecular fluorine,[77] (36.94 ±0.14) kcal mol^{-1}, was the subject of some controversy until 1975,[78–86] but is now firmly established, see Table 9. An empirical fit to the temperature dependence[86] of the equilibrium constant is given by Eq. (22):

$$K_e(\text{mole cm}^3) = 1.855 \times 10^1 \, e^{-18920/T}. \qquad (22)$$

The loss of F atoms via homogeneous three-body and heterogeneous (wall) recombinations, however, is not nearly as well characterized as the dissociation energy. There have only been a handful of reports describing third-order F+F+M recombination rate constant measurements,[87–89] and even fewer studies exploring wall effects,[86,90] see Table

10. Perhaps not surprisingly, theoretical estimates[91,92] for $k_{\text{recombination}}$ vary widely—from 2.7×10^{-32} to 5.2×10^{-35} cm^6 molecule^{-2} s^{-1}.

The lack of kinetic data for the recombination process has long been recognized. In his 1971 review of F_2 dissociation–recombination kinetics, Lloyd[92] could not find any experimental studies of F atom recombination, and bases his recommendation of $k \approx 10^{-34}$ cm^6 molecule^{-2} s^{-1} on the theoretical method of Benson and Fueno.[93] The 1977 Aerospace review[1] also recommended $\sim 10^{-34}$ cm^6 molecule^{-2} s^{-1} based on their expression for the dissociation rate constant, $(8.3 \times 10^{-11} A_M \exp(-35\,100/RT)$ cm^3 molecules^{-1} s^{-1}, where A_M depends on the collider) and a theoretical calculation by Shui et al.[94] The only experimental measurement available at the time[88] suggested $k(\text{Ar}) = 8.0 \times 10^{-35}$ cm^6 molecule^{-2} s^{-1}, a factor of 3 smaller than the recommended value. However, this measurement used Cl atom recombination emission and $F + Cl_2$ titrations to determine [F]. This method is susceptible to error because of the complexity of halogen atom recombination processes.[95] In fact, Clyne and Stedman[96] have shown that the red emission generated by recombining Cl atoms is not necessarily proportional to [Cl]^2, but has a much more complex dependence on [Cl] and a third body [M]. As a result, the measured $k(\text{Ar})$ may be significantly in error. A more reliable electron spin resonance (ESR) measurement by Ultee[89] found $k(\text{He}) = (6 \pm 1) \times 10^{-34}$ cm^6 molecule^{-2} s^{-1} and $k(\text{Ar}) < k(\text{He}) < k(F_2)$. A very recent electron paramagnetic resonance (EPR) measurement by Vasilev et al.[86] for F_2 is in reasonable agreement with $k(F_2) = (4.7 \pm 1.2) \times 10^{-34}$ cm^6 molecule^{-2} s^{-1}. In lieu of more data, we recommend the results of Ultee[89] and Vasilev[86] for He and F_2 and suggest $k(\text{Ar}) = 1/2k(\text{He})$.

Because F_2 plasma reactors are often used by the microelectronic industry for etching silicon wafers, the rate constant and mechanisms for heterogeneous F atom recombination has become a topic of increasing interest in the last few years.[90] In general, the probability of F atom recombination at a surface is small relative to other halogens ($\gamma_F \leqslant 0.05$, $\gamma_{Cl} > 0.6$) and the mechanism seems to be a two step process where an atom initially adsorbs onto the surface and is removed following reaction with another halogen atom. Although two independent laboratories have shown that F atoms have small recombination probabilities, this parameter may vary significantly from experiment to experiment, depending on the type of material and any coatings. The rec-

TABLE 10. Experimental third-order recombination rate constants for $F+F+M \rightarrow F_2+M$

Collision partner	Temperature (K)	Rate constant (cm^6 molecules^{-2} s^{-1})	Reference
Ar	300	8.0±0.6×10^{-35}	Ganguli and Kaufman[88]
Ar[a]	300	3.7±1.1×10^{-35}	Baulch et al.[28]
He	300	≤4.1×10^{-33}	Valance et al.[87]
He[b]	300	6±1×10^{-34}	Ultee[89]
F_2	300	4.7±1.2×10^{-34}	Vasiliev et al.[86]

[a]Extrapolated beyond recommended temperature range (1400–2600 K).
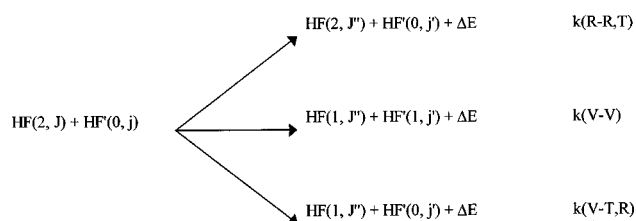[b]Preliminary data indicated $k_{Ar} < k_{He} < k_{F2}$.

FIG. 4. HF self-relaxation pathways. The $V–V$, $R–R,T$, and $V–T,R$ pathways are shown for an HF molecule with $v=2$ and an arbitrary J state colliding with an HF molecule in the ground vibrational state. Note that due to conservation of energy constraints, only the $V–T,R$ pathway can produce high rotational states in the product HF(v,J) molecule, see Fig. 5.

FIG. 5. Detailed near-resonant $V–T,R$ relaxation pathways. The distinction between ''true'' $V–T,R$ energy transfer and $V–R$ redistribution is shown by the solid and broken lines, respectively. Numerous combinations of HF(1,J) and HF(0,J) states can be populated by HF $V–T,R$ energy transfer. Because of the presence of near-resonant energy levels in $v=1$ and 0, $V–R$ redistribution can populate high rotational states of $v=0$ and 1. For example, the near resonant $V–R$ redistribution pathways shown in the figure have energy defects of -46.9, 519.6, and 273.7 cm^{-1}, for relaxation to (1, 15), (1, 14) and (0, 20), respectively. On the other hand, if HF(2, 6) is relaxed to HF(1, 6) by HF(0,J), up to eight quanta of rotational energy can be transferred to the HF($v=0$), molecule.

ommendations of Vasilev[86] and Kota[90] should be used with caution.

2.4. Rotational Nonequilibrium

The question of rotational nonequilibrium for the HF laser system has been the subject of considerable controversy for many years.[97] The presence of rotational nonequilibrium in the HF laser was first suggested by pulse initiated HF laser experiments by Pimentel and co-workers,[98,99] which generated lasing on HF rotational transitions with J as high as 33 in the $v=1$ manifold and $J=29$ in the $v=0$ manifold. The observation of rotational laser emission is an extremely sensitive method for studying rotational occupancies because the population inversions needed to produce the laser emission are 100 times lower than for rovibrational transitions.[99] Pimentel's analysis of the transient behavior of the laser emission suggested that collisional $V–T,R$ energy transfer reactions that populate the high rotational states were responsible for the observed positive gain, rather than direct pumping by the initiating reaction. A remarkably similar phenomenon was observed by Robinson and co-workers in their work with HF,[100] OH,[101] and NH.[102] Further experimental observations of emission from high J states following HF(v) quenching by CO, CO_2, and HCN,[103] as well as quasiclassical trajectory calculations[104] also support the assertion that high rotational states are produced in the $V–T,R$ relaxation process.

The evidence is clear that the principal HF(v) relaxation mechanism in the HF laser environment is HF self-relaxation, and that the relaxation proceeds via $V–T,R$ energy transfer (see Sec. 2.2.3). There are two important questions, however, that remain:

(1) What are the specific products of the $V–T,R$ process? Figures 4 and 5 summarize the possible relaxation/energy transfer routes for HF($v=2$). The possible mechanisms include ''true'' $V–T,R$ relaxation (the solid arrow in Fig. 5) where the loss of a vibrational quantum results in some small amount of rotational and translational energy transfer to the HF($v=0$) quencher or near-resonant $V–R$ redistribution (the broken arrows in Fig. 5), where the quenched HF molecule relaxes to a lower vibrational state with a high rotational quantum number and very little energy is transferred to the quencher.
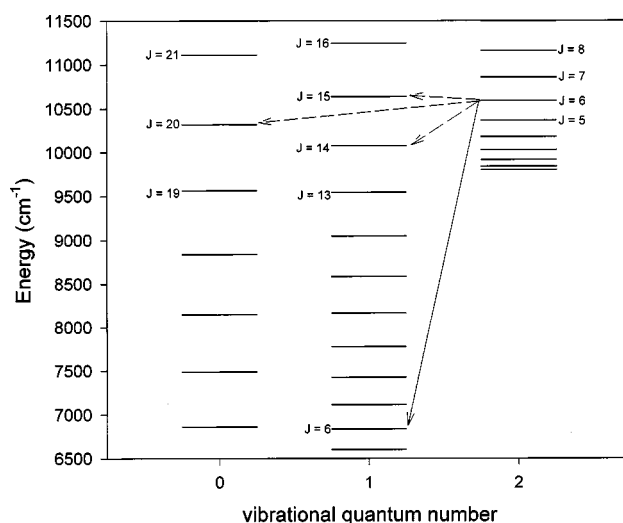
(2) Are the high-J HF molecules produced by the self-relaxation process ''metastable''? In general, rotational relaxation rate constants ($k \sim 10^{-10}$–10^{-9} cm^3 molecules^{-1} s^{-1}) are 10–100 times larger than vibrational deactivation rate constants ($k \sim 10^{-12}$–10^{-10} cm^3 molecules^{-1} s^{-1}). However, because the separation between HF rotational levels is large, it is possible that $k_{R–R,T} \approx k_{V–R,T}$ for sufficiently high J levels. If so, the vibrational relaxation process could significantly perturb the equilibrium rotational distribution and considerable errors could be realized when attempting to model real HF laser devices.

2.4.1. Relevant Experimental Studies

As was discussed in Sec. 2.2.3.1 above, the self-relaxation measurements of Crim,[48] Kaufman,[52] and Moore[62] all concluded that multiquantum deactivations were not important. In particular, Crim determined that 0.98 ± 0.19 and 0.87 ± 0.21 of the relaxed HF(4) and HF(5) molecules, respectively, appear in the next lower vibrational level.[48] Kaufman came to the same conclusion and suggested that multiquantum relaxation processes account for less than 1% of the total measured relaxation rate constants. Thus, any high-J states that are produced by the HF(v) self-relaxation process will almost certainly be found in the $J=10–20$ range of the next lower vibrational level.

The role of $V–T,R$ relaxation reactions that populate high rotational states of the next lower vibrational level was addressed directly by the work of Haugen et al.[105] who measured the time dependent population of HF($v=0$,J

TABLE 11. Rate constants for rotational relaxation of HF($v = 0, J = 13$)[107]

Collision partner	Rate constant ($\times 10^{-12}$ cm^3 molecules^{-1} s^{-1})
He	13 ± 2
Ne	2.2 ± 0.4
Ar	0.93 ± 0.09
Kr	4.4 ± 0.5
Xe	6.2 ± 0.6
H$_2$	110 ± 20
D$_2$	120 ± 20
HF	182 ± 10
HF	62 ± 31[a]

[a]See Ref. 105.

$= 10\text{--}14$) following pulsed generation of HF($v = 1, J = 6$). They concluded that a substantial fraction of the relaxation of $v = 1$ occurs through the high lying rotational levels of $v = 0$ ($\sim 20\%\text{--}40\%$ of the total $v = 1$ relaxation rate). The total phenomenological self-relaxation rate constant for HF($v = 1$) (which by definition for $v = 1$ is purely $V\text{--}T, R$) that they measured was identical to that determined in the double resonance experiments of Crim and co-workers,[48] ($k = 1.46 \pm 0.1 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}).

There has been a significant effort in the last 20 years to measure and predict rotational relaxation rate constants. Most recently, Muyskens *et al.*[106] have measured rotational relaxation rate constants for HF($v = 2\text{--}4, J = 0\text{--}4$) with a variety of colliders. Their results generally confirm the standard view that rotational relaxation is 10–100 times faster than vibrational relaxation, particularly for the lower rotational quantum numbers ($J = 0\text{--}8$). In addition to probing the role of $V\text{--}T, R$ relaxation the Leone group[105] also measured rotational relaxation rate constants for $v = 0$, $J = 10\text{--}14$. They found no experimental evidence of bottleneck effects and concluded that $R\text{--}R, T$ rates always exceed the $V\text{--}T, R$ rate by 1 or 2 orders of magnitude, even for $J = 10\text{--}13$. While their initial report[105] recommended $R\text{--}R, T$ rate constants for $v = 0$, $J = 10\text{--}14$ which range from $\sim 1.2 \times 10^{-10}$ to 6×10^{-11} cm^3 molecules^{-1} s^{-1}, subsequent measurements in the same laboratory suggested even larger values.[107,108] The dominance of $R\text{--}R, T$ relaxation over $V\text{--}T, R$ and $V\text{--}V$ energy transfer extends to other colliders besides HF. For example, Taatjes and Leone measured the rotational relaxation rate constants for HF with a variety of collision partners (Ar, He, Ne, Kr, Xe, H$_2$, and D$_2$)[107] and the results for HF($v = 1, J = 13$) are summarized in Table 11. Clearly, rotational relaxation by atomic species is very inefficient relative to HF, H$_2$, and D$_2$. In all cases, however, the rotational relaxation rate constants for atomic quenchers exceed the vibrational deactivation rate constants by several orders of magnitude: $k(R\text{--}R, T) \geqslant 10^{-12}$ and $k(V\text{--}R, T) = 10^{-17}\text{--}10^{-18}$ cm^3 molecules^{-1} s^{-1}. Leone and co-workers extended their measurements to nonambient temperatures[108] and found that the HF$V\text{--}T, R$ and $R\text{--}R, T$ self-relaxation reactions have a negative temperature dependence. The negative temperature dependence for rotational relaxation of HF($v = 0, J = 13$) is dramatic, $T^{-1.57}$.

In addition to the direct experimental measurements, there have also been attempts to extrapolate the low-J results to high-J using scaling laws and approximations such as the exponential energy gap (EEG) law, the power law model (PLM), and the energy corrected sudden (ECS) approximation. Most of these efforts are summarized elsewhere,[97] and while the accuracy of the models for predicting accurate $R\text{--}R, T$ rates is the subject of some controversy, two general conclusions may be drawn from the relevant literature. (1) The PLM and ECS models give the most reliable results when compared to the existing high J and low J data. The EEG model consistently underestimates $k(R\text{--}R, T)$, in some cases by several orders of magnitude. (2) The rate constants for rotational relaxation, $k(R\text{--}R, T)$, are large, $\geqslant 10^{-11}$ cm^3 molecules^{-1} s^{-1}.

One noteworthy report,[109] which claims to use a ''more reliable form of the power scaling law'' to calculate rotational energy transfer rate constants for $v = 1\text{--}2$, $J = 0\text{--}20$ gives $k(R\text{--}RT)$ values on the order of $10^{-11}\text{--}10^{-10}$ cm^3 molecules^{-1} s^{-1}, even for $J = 20$. On the other hand, their results suggest that rotational relaxation rates actually *increase* with vibrational energy, contrary to the results of Crim and co-workers.[106] The reliability of their model is, as the authors themselves admit, ''an open discussion.''

2.4.2. Relevant Theoretical Studies

No review of the role of rotational equilibrium for the HF laser would be complete without some discussion of quasi-classical trajectory calculation results, most notably those of Wilkins and Kwok,[64,110] Thompson,[104,111] and Billing.[66,112] Billing's calculations found no evidence of high rotational state population, while the calculations by Wilkins and Thompson indicate that vibrational–rotational energy transfer is a relatively efficient process and that multiquantum deactivations occur on a fairly regular basis. In particular, Thompson[104] calculated state-to-state collsion cross sections for HF($v = 4, J = 20$) relaxation by He and reported 3.3, 6.7, 10.7, 18.5, and 38.24 a.u.^{2} for $\Delta v = 4$, 3, 2, 1, and 0, respectively. Calculations of this sort are usually very sensitive to the details of the potential surface on which the trajectories run, and unfortunately the requisite state-to-state cross sections required to evaluate the reliability of the theoretical calculations have yet to be measured. In general, the available experimental data contradict the theory and do not support multiquantum deactivations.

In summary, the majority of the available evidence supports single vibrational quantum $V\text{--}T, R$ relaxation which populates the high rotational states of the next lower vibrational state. There is no specific experimental evidence supporting multiquantum vibrational $V\text{--}T, R$ relaxation. There is no doubt that near-resonant $V\text{--}T, R$ relaxation plays an important role in the HF chemical laser system and successful quantitative modeling depends on its inclusion. However, the available experimental evidence clearly shows that $k(V\text{--}T, R) \ll k(R\text{--}R, T)$, and in light of this, it is doubtful that high J states can act as ''reservoirs'' for near-resonant

TABLE 12. Recommended rate constants for the HF laser system

| Reaction | Recommended rate constant expression | | Relevant references |
	Equation	$g(v)$	
$F+H_2 \rightarrow HF+H$	$T=190-376$ K: $g(v)*1.1\pm0.1\times10^{-10}e^{-(450\pm50)/T}$ $T>376$ K: $g(v)*2.2\pm0.4\times10^{-10}e^{-(595\pm50)/T}$	$g(0)=0.00$, $g(1)=0.15$ $g(2)=0.55$, $g(3)=0.30$	3, 34, 38
$H+F_2 \rightarrow HF+F$	$g(v)*5.0\times10^{-15}T^{1.5}e^{-845/T}$	See Table 5	3, 17–19, 22, 23
$H+HF(v) \rightarrow H_2(v')+F$	$v=3$ $3.0\times10^{-11}T^{0.179}e^{-382/T}$ $v=4-6$ $g(v,v')*1.0\times10^{-10}e^{-252/T}$	$g(4,0)=g(4,1)=0.5$, $g(5,0)=0.5$, $g(5,1)=1.0$, $g(6,0)=g(6,1)=0.5$, $g(6,2)=1.5$	3, 41–44
$HF(v)+H_2 \rightarrow HF(v')+H_2$	$g(v)*1.0\times10^{-12}$	See Table 8	3, 23, 56, 68–71
$HF(v)+H_2(v') \rightarrow HF(v-1)+H_2(1)$	$5.2\pm0.4\times10^{-13}$	$v=1$ only, see p. 17	3, 23, 56, 68–71
$HF(v)+H \rightarrow HF(v')+H$	$A(v)*1.7\times10^{-8}T^{-1}$ $+$ $B(v)*1.7\times10^{-12}e^{-352/T}$	$A(3)=1.4$, $A(4)=2.0$, $A(5)=2.7$, $A(6)=3.5$ $B(1)=0.4$, $B(2-6)=0.7$	3, 41, 42
$HF(v)+F \rightarrow HF(v-1)+F$	$g(v)*2.7\times10^{-11}e^{-1359/T}$	$g(v)=v$	3, 73–75
$HF(v)+M \rightarrow HF(v-1)+M$	$A(M)*1.7\times10^{-29}*v*T^{4.5}$	$A(Ar)=2.0$ $A(F_2)=2.0$ $A(He)=3.7$	3, 76
$HF(v)+HF \rightarrow HF(v')+HF$	$v=1-5$: $k_c*A(v)T^{-1.3}$ $v=6$,[a] 300 K: 2.9×10^{-10} $v=7$,[a] 300 K: 4.5×10^{-10}	$k_c=\pi\sigma^2\sqrt{\dfrac{8RT}{\pi\mu}}$ $A(1)=12.0$, $A(2)=218.0$, $A(3)=315.2$, $A(4)=764.0$, $A(5)=1610.3$	46, 48, 50
$HF(v)+HF(v') \rightarrow HF(v+1)+HF(v'-1)$	$(v+1)^{0.35}4.5\times10^{-9}T^{-1}$		3, 15
$F+F+M \rightarrow F_2+M$	$M\times10^{-34}$	$M(He)=6\pm1$ $M(F_2)=4.7\pm1.2$ $M(Ar)\sim3$	86, 89

[a]The temperature dependence of HF(6-7)+HF has not been measured. If the $T^{-1.3}$ dependence and the expression used for $v=1-5$ holds, then $A(6)=3107$ and $A(7)=4339$.

lasing levels. It seems more likely that the $V-T,R$ process simply reduces the gain of the (1-0) and (2-1) transitions by reducing the population of the upper state while simultaneously increasing the population of the lower state.

3. Conclusions

Table 12 summarizes the recommendations of this paper. Overall, many of the expressions found in the 1982 review by Cohen and Bott[3] remain valid today, in particular, the elimination of multiquantum deactivation reactions that were a key feature of the 1977 kinetics package. These kinds of relaxation processes have been demonstrated to be very slow and can be safely neglected. Other areas of agreement include the total HF generation rate constants and the relaxation rate constants for collisions with molecular and atomic

quenchers. A new measurement of the H atom removal rate constant for the "hot" reaction, $H+F_2$, would be particularly useful.

The major changes that we suggest occur in the Einstein coefficients, HF self-relaxation, and the nascent distribution for $H+F_2$. While in many cases these changes are minor, they may ultimately have significant effects to CFD calculation results due to enormous complexity of the HF laser system.

Clearly, there are some aspects of the HF kinetics package that should be re-examined experimentally. For example, in the case of $HF(v)+F$, H, Ar, and He, the recommended expressions are based on only a handful of measurements at a narrow range of temperatures. While the role of multiquantum deactivations is very small according to the available experimental data, some believe[5] that the $v^{2.9}$ scaling law for the HF self-relaxation process may be indicative of open

multiquantum deactivation relaxation pathways, particularly for high v. Direct measurements for the Treanor pumping (reaction (14)) rate constants are also needed, particularly for $HF(v>1)+HF(v>1)$, for which no data currently exists. Clarification of these issues would undoubtedly significantly enhance our understanding of the HF laser.

4. Acknowledgments

5. References

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